Connecting Binuclear Pd(III) and Mononuclear Pd(IV) Chemistry by Pd–Pd Bond Cleavage

Supporting Information

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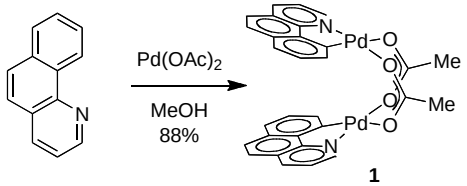
Materials and Methods

Reactions were carried out under ambient atmosphere unless otherwise specified. Anhydrous solvents were obtained either by filtration through drying columns[i] (ether, CH_2Cl_2, THF) on an mBraun system or by distillation over sodium (ether, pentane). Purified compounds were further dried under high vacuum (0.01–0.05 Torr). Yields refer to purified and spectroscopically pure compounds unless otherwise noted. NMR spectra were recorded on either a Varian Unity/Inova 600 spectrometer operating at 600 MHz for ^{1}H acquisitions, a Varian Unity/Inova 500 spectrometer operating at 500 MHz and 125 MHz for ^{1}H and ^{13}C acquisitions, respectively, or a Varian Mercury 400 spectrometer operating at 400 HMz and 375 MHz for ^{1}H and ^{19}F acquisitions, respectively. Chemical shifts are reported in ppm with the solvent resonance as the internal standard. The following solvent chemical shifts were used as reference values (ppm): $CDCl_3$ = 7.26 (^{1}H), 77.0 (^{13}C); CD_2Cl_2 = 5.32 (^{1}H), 53.8 (^{13}C); $C_2D_4Cl_2$ = 3.72 (^{1}H); benzene-d_6 = 7.15 (^{1}H), 128.0 (^{13}C). Data is reported as follows: s = singlet, br = broad, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constants in Hz; integration. UV-vis spectra were obtained on a Varian Cary 50 Probe UV-visible spectrophotometer. High-resolution mass spectra were obtained on Jeol AX-505 or SX-102 spectrometers at the Harvard University Mass Spectrometry Facilities. $Pd(OAc)_2$ was purchased from Strem. XeF_2 was purchased from Matrix Scientific. Benzo[*h*]quinoline was obtained from TCI America. 2-Iodobenzoic acid was obtained from Sigma Aldrich. All other chemicals were used without purification.

Experimental Data

Experimental Procedures and Compound Characterization

Benzo[*h*]quinolinyl palladium acetate dimer (1)



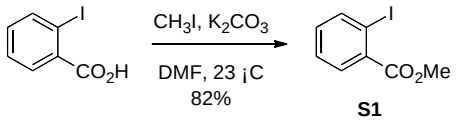
1

Complex **1** was prepared according to a published procedure.[2] To benzo[*h*]quinoline (1.00 g, 5.58 mmol, 1.00 equiv) in MeOH (75 mL) at 23 ºC was added $Pd(OAc)_2$ (1.25 g, 5.58 mmol, 1.00 equiv). After 8 h, the precipitate was isolated by filtration and washed sequentially with MeOH (50 mL) and Et_2O (50 mL). The solid was dissolved in CH_2Cl_2 (250 mL) and filtered through a plug of Celite. Solvent was removed in vacuo to afford 1.68 g of the title compound as a yellow solid (88% yield).

NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.82 (dd, *J* = 5.0 Hz, 1.1 Hz, 2H), 7.44 (dd, *J* = 8.0 Hz, 1.1 Hz, 2H), 7.25–7.20 (m, 6H), 7.09 (dd, *J* = 6.9 Hz, 1.1 Hz, 2H), 6.98 (d, *J* = 8.7 Hz, 2H), 6.48 (dd, *J* = 8.0 Hz, 5.0 Hz, 2H), 2.38 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 182.3, 152.9,

148.6, 148.5, 139.7, 135.0, 132.2, 128.7, 127.6, 127.4, 124.7, 122.6, 121.8, 119.5, 24.9. These spectroscopic data correspond to those reported in the literature.[ii] UV-vis Spectroscopy (CH_2Cl_2, 23 ˚C): 425 nm ($\varepsilon = 2.00 \times 10^3$ M^{-1} cm^{-1}); 376 nm ($\varepsilon = 4.30 \times 10^3$ M^{-1} cm^{-1}); 346 nm ($\varepsilon = 4.18 \times 10^3$ M^{-1} cm^{-1}). Mass Spectrometry: LRMS-APCI (m/z): 686.0 [$C_{30}H_{22}N_2O_4Pd_2^+$]. Cyclic voltammogram included in Electrochemical Data Section. X-ray data has been submitted to the Cambridge Crystal Structure Database as CCDC 705005 and CCDC 832191.

Methyl 2-iodobenzoate (S1)

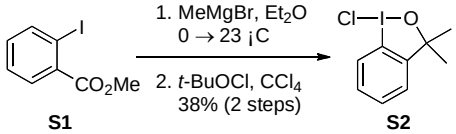


S1

Compound **S1** was prepared according to a published procedure.[4] To 2-iodobenzoic acid (100.0 g, 0.4032 mol, 1.000 equiv) in DMF (300 mL) at 23 ºC was added K_2CO_3 (66.84 g, 0.4836 mol, 1.199 equiv). After gas evolution ceased, CH_3I (27.60 mL, 62.93 g, 0.4433 mol, 1.099 equiv) was added and the reaction mixture was stirred at 23 ºC for 14 h. The reaction mixture was added to H_2O (300 mL) and the aqueous phase was extracted with Et_2O (3 × 100 mL). The organic layers were combined, washed with H_2O (2 × 100 mL), brine (1 × 50 mL), and dried with $MgSO_4$. Solvent was removed in vacuo to afford 86.59 g of the title compound as a yellow oil (82% yield).

R_f = 0.39 (hexanes/EtOAc 9:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.99 (d, *J* = 7.9 Hz, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.39 (dd, *J* = 7.5 Hz, 0.7 Hz, 1H), 7.14 (dd, *J* = 7.6 Hz, 1.6 Hz, 1H), 3.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 23 ºC, δ): 166.9, 141.3, 135.0, 132.6, 130.9, 127.8, 94.0, 52.4. These spectroscopic data correspond to those reported in the literature.[iii]

1-Chloro-1,3-dihydro-3,3-dimethyl-1,2-benziodoxole (S2)

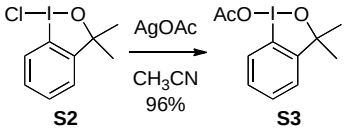


S1 **S2**

Compound **S2** was prepared according to a published procedure.[5] To methyl 2-iodobenzoate (**S1**) (10.0 g, 38.2 mmol, 1.00 equiv) in Et_2O (200 mL) at 0 ºC under an N_2 atmosphere was added MeMgBr (3.0 M in Et_2O, 28 mL, 84 mmol, 2.2 equiv) over 30 min. The reaction mixture was stirred for 30 min, warmed to 23 ºC and stirred for an additional 2 h. The reaction mixture was extracted with Et_2O (3 × 50 mL). The organic layers were combined, washed with H_2O (2 × 100 mL), brine (1 × 50 mL), and dried with $MgSO_4$. Solvent was removed in vacuo. The residue was taken up in CCl_4 (20 mL) and *tert*-butyl hypochorite (7.10 mL, 6.82 g, 63.0 mmol, 1.20 equiv) was added in one portion. The reaction mixture was stirred at 23 ºC. After one hour the precipitate was collected by filtration and washed with hexane (30 mL) to afford 4.26 g of the title compound as a yellow solid (38% yield).

NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 8.02 (dd, *J* = 8.3 Hz, 1.0 Hz, 1H), 7.57 (ddd, *J* = 8.3 Hz, 8.3 Hz, 1.6 Hz, 1H), 7.52 (ddd, *J* = 7.3 Hz, 7.3 Hz, 1.2 Hz, 1H), 7.17 (dd, *J* = 7.3 Hz, 1.6 Hz, 1H), 1.55 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 23 ºC, δ): 149.4, 130.9, 130.4, 128.4, 126.1, 114.6, 85.1, 29.2. These spectroscopic data correspond to those reported in the literature.[iv]

1-Acetoxy-1,3-dihydro-3,3-dimethyl-1,2-benziodoxole (S3)

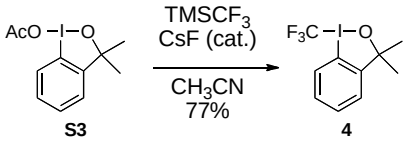


S2 **S3**

Compound **S3** was prepared according to a published procedure.[6] This reaction was carried out in a nitrogen-filled dry box. To 1-chloro-1,3-dihydro-3,3-dimethyl-1,2-benziodoxole (**S2**) (3.00 g, 10.1 mmol, 1.00 equiv) in CH_3CN (40 mL) at 23 ºC was added AgOAc (1.68 g, 10.1 mmol, 1.00 equiv) as a solid in one portion. The reaction mixture was stirred for 16 h at 23 ºC in the dark. The reaction mixture was filtered through a pad of celite. The filtrate was concentrated in vacuo to afford 3.11 g of the title compound as a colorless solid (96% yield).

NMR Spectroscopy: ^{1}H NMR (400 MHz, benzene-d_6, 23 ºC, δ): 7.81 (d, *J* = 8.1 Hz, 1H), 6.95 (ddd, *J* = 7.3 Hz, 7.3 Hz, 1.5 Hz, 1H), 6.88 (ddd, *J* = 7.3 Hz, 7.3 Hz, 1.1 Hz, 1H), 6.56 (dd, *J* = 7.3 Hz, 1.1 Hz, 1H), 1.94 (s, 3H), 1.28 (s, 6H). ^{13}C NMR (100 MHz, benzene-d_6, 23 ºC, δ): 176.2, 150.1, 130.4, 130.1, 129.6, 126.1, 116.3, 84.2, 29.2, 21.2. These spectroscopic data correspond to those reported in the literature.[v]

1-Trifluoromethyl-1,3-dihydro-3,3-dimethyl-1,2-benziodoxole (4)

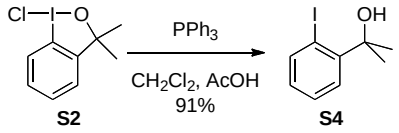


S3 **4**

Compound **4** was prepared according to a published procedure.[6] To 1-acetoxy-1,3-dihydro-3,3-dimethyl-1,2-benziodoxole (**S3**) (1.10 g, 3.44 mmol, 1.00 equiv) in CH_3CN (20 mL) at 23 ºC was added $TMSCF_3$ (0.770 mL, 0.732 g, 5.15 mmol, 1.50 equiv) in one portion. CsF (50 mg, 0.33 mmol, 0.096 equiv) was added and the reaction mixture was stirred for 16 h at 23 ºC in the dark. Solvent was removed in vacuo and pentane (50 mL) was added. The reaction mixture was filtered through a pad of celite. The filtrate was concentrated in vacuo to afford 877 mg of the title compound as a yellow solid (77% yield).

NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.54–7.51 (m, 2H), 7.44–7.38 (m, 2H), 1.48 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 149.2, 130.6, 129.8, 127.9 (q, *J* = 3.0 Hz), 127.80, 110.5 (q, *J* = 3.1 Hz), 109.0 (q, *J* = 210.5 Hz), 76.5, 30.8. ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –39.5. These spectroscopic data correspond to those reported in the literature.[6]

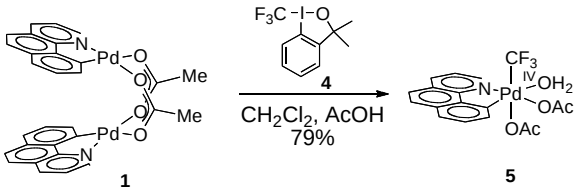
2-(2-iodophenyl)propan-2-ol (S4)



To 1-chloro-1,3-dihydro-3,3-dimethyl-1,2-benziodoxole (**S2**) (256 mg, 0.863 mmol, 1.00 equiv) in CH_2Cl_2 (8 mL) and AcOH (0.1 mL) at 23 ºC was added PPh_3 (226 mg, 0.863 mmol, 1.00 equiv) as a solid in one portion. The reaction mixture was stirred for 5 min at 23 ºC before solvent was removed in vacuo. The residue was purified by chromatography on SiO_2 gel eluting with EtOAc / hexanes (1 : 9 (v/v)) to afford 206 mg of the title compound as a pale yellow oil (91% yield).

R_f = 0.47 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.96 (dd, *J* = 7.9 Hz, 1.5 Hz, 1H), 7.62 (dd, *J* = 7.9 Hz, 1.6 Hz, 1H), 7.33 (ddd, *J* = 8.6 Hz, 7.2 Hz, 1.3 Hz, 1H), 6.90 (ddd, *J* = 8.9 Hz, 7.3 Hz, 1.8 Hz, 1H), 1.76 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 148.4, 142.7, 128.6, 128.1, 126.7, 93.1, 73.56, 29.8. These spectroscopic data correspond to those reported in the literature.[vi]

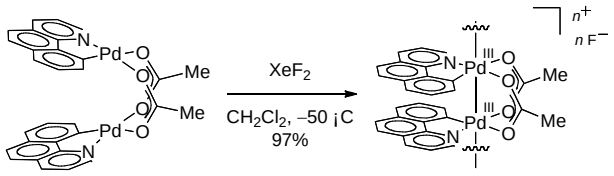
Benzo[*h*]quinolinyl trifluromethyl palladium(IV) diacetate aquo complex (5)



Compound **5** was prepared according to a published procedure.[8] To benzo[*h*]quinolinyl palladium acetate dimer (**1**) (552 mg, 0.803 mmol, 1.00 equiv) in CH_2Cl_2 (15 mL) at 23 ºC was added AcOH (0.92 mL, 970 mg, 16 mmol, 20 equiv) and 1-trifluoromethyl-1,3-dihydro-3,3-dimethyl-1,2-benziodoxole (**4**) (1.06 g, 3.21 mmol, 4.00 equiv), sequentially. The reaction mixture was stirred at 23 ºC for 15 min before solvent was removed in vacuo. The residue was dissolved in CH_2Cl_2 (5 mL) and hexanes (40 mL) was added. The precipitate was isolated by filtration on a plug of celite and was washed with hexanes (100 mL). The residue was recovered from the celite plug with Et_2O (200 mL). Solvent was removed in vacuo to afford 620 mg of the title compound as a green solid (79% yield).

NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 9.67 (br s, 2H), 9.06 (d, *J* = 5.3 Hz, 1H), 8.52 (dd, *J* = 8.1 Hz, 1.0 Hz, 1H), 7.99 (d, *J* = 7.6 Hz, 1H), 7.97 (d, *J* = 8.8 Hz, 1H), 7.92 (d, *J* = 7.9 Hz, 1H), 7.81 (d, *J* = 8.6 Hz, 1H), 7.77–7.74 (m, 2H), 2.34 (s, 3H), 1.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 23 ºC, δ): 151.3, 147.4, 139.4, 136.2, 135.5, 130.9, 129.5, 128.6, 126.4, 126.1, 124.3, 122.9, 24.6, 24.2. ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –23.7. These spectroscopic data correspond to those reported in the literature.[vii] X-ray data has been submitted to the Cambridge Crystal Structure Database as CCDC 831838.

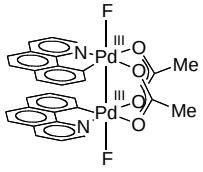
Palladium(III) fluoride 8



1 **8**

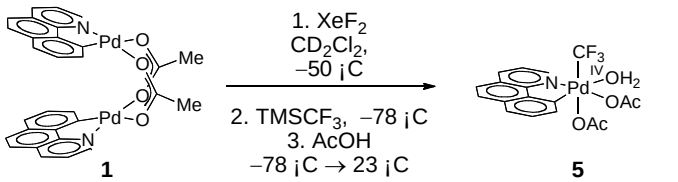
Compound **8** was prepared according to a published procedure.[9] All manipulations were carried out in a dry box under a N_2 atmosphere. Benzo[*h*]quinolinyl palladium acetate dimer (**1**) (21 mg, 3.1×10^{-5} mol, 1.0 equiv) was dissolved in 1.0 mL CH_2Cl_2 at –50 ˚C. XeF_2 (5.3 mg, 3.1×10^{-5} mol, 1.0 equiv) was added as a solid in one portion. The yellow solution immediately became a dark red-brown suspension. After stirring for five min at –50 ˚C, solvent was removed in vacuo at –50 °C. The residue was washed with Et_2O (1.0 mL) at –50 ˚C. The Et_2O was decanted, and the residue was dried under vacuum at –50 °C to afford 22 mg of the title compound (97% yield) as a dark red solid.

NMR Spectroscopy: ^{1}H-NMR (500 MHz, CD_2Cl_2, –10 ºC, δ): 7.87 (d, *J* = 5.1 Hz, 2H), 7.71 (d, *J* = 7.7 Hz, 2H), 7.47–7.40 (m, 4H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 7.0 Hz, 2H), 7.15 (d, *J* = 8.8 Hz, 2H), 6.86 (dd, *J* = 4.8 Hz, *J* = 4.8 Hz, 2H), 2.72 (s, 6H). ^{19}F-NMR (375 MHz, CD_2Cl_2, –10 ºC, δ): –170.4 (br s, $h_{1/2}$ = 317.8 Hz). UV-VIS Spectroscopy (CH_2Cl_2, 0 ˚C): 1021 nm (absorbance at this wavelength is non-linear with concentration); 464 nm (absorbance at this wavelength is non-linear with concentration); 376 nm ($\varepsilon = 2.47 \times 10^3$ M^{-1} cm^{-1}). ^{13}C NMR signals were not observed due to signal broadness. The reported spectral data correspond to those reported in the literature.[viii] In addition to compound **8**, the structure of which has been submitted to the Cambridge Crystal Structure Database (CCDC 841654), complex **S5**, in which the fluoride ligands are Pd-bound, have also been characterized (CCDC 841653). In solution, extended chain **8** is exclusively observed.



S5

Observation of 5 from Treatment of 8 with AcOH



1 **5**
61-98% based on **1**

This reaction was carried out in a nitrogen-filled dry box. To benzo[*h*]quinolinyl palladium acetate dimer

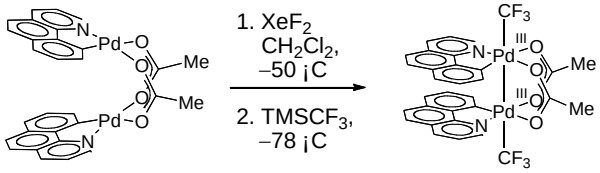
(**1**) (45.1 mg, 6.56×10^{-5} mol, 1.00 equiv) in CH_2Cl_2 (2.0 mL) at –50 ºC was added XeF_2 (11.1 mg, 6.56×10^{-5} mol, 1.00 equiv) as a solid in one portion. After 45 min, the reaction was cooled to –78 ºC and $TMSCF_3$ (29.5 μL, 28.0 mg, 0.196 mmol, 3.00 equiv) was added. The reaction vessel was removed from the cold bath and allowed to briefly warm until the color of the reaction mixture was observed to change from red to dark brown green. The reaction mixture was re-cooled to –78 ºC. After one minute, AcOH (38.0 μL, 39.9 mg, 0.656 mmol, 10.0 equiv) was added to the reaction mixture and the reaction mixture was warmed to 23 ºC. ^{1}H and ^{19}F NMR spectra were obtained which confirmed the formation of **5**. Mesitylene (3.0 μL, 2.6 mg, 2.2×10^{-5} mol, 0.33 equiv) was added and the amount of **5** formed was quantified by comparison of the integral of mesitylene at 6.78 ppm with the integral of **5** at 8.52 ppm. Yields of 61–98% based on **1** were observed. The yields of TMSF and CF_3H (40–52% and 21–30%) were determined by integration of ^{19}F NMR signals versus added 1-bromo-4-(trifluoromethyl)benzene.

The spectral data (^{1}H and ^{19}F NMR) of the **5** obtained by the above procedure is identical to authentic material and ^{1}H and ^{19}F peaks were coincident with the peaks of an authentic sample of **5** added to the NMR sample prepared above.[ix] Spectral data of compound **1** obtained by this procedure is identical to that of an authentic sample prepared above.

CHF_3: NMR Spectroscopy: ^{19}F NMR (375 MHz, CD_2Cl_2, –80 ºC, δ): –76.5 (d, J = 77.8 Hz).

TMSF: NMR Spectroscopy: ^{1}H-NMR (400 MHz, CD_2Cl_2, 23 ºC, δ): 0.21 (d, J = 8.8 Hz, 9H). ^{19}F-NMR (375 MHz, CD_2Cl_2, 23 ºC, δ): –160.3. ^{29}Si-NMR (80 MHz, CD_2Cl_2, 23 ºC, δ) 31.3 (d, J = 273 Hz).

Observation of Benzo[*h*]quinolinyl trifluoromethyl palladium(III) acetate dimer (9)



1 **9**

The following reaction was carried out in an N_2-filled dry box. To benzo[*h*]quinolinyl palladium acetate dimer (**1**) (12.9 mg, 1.88×10^{-5} mol, 1.00 equiv) in CD_2Cl_2 (0.8 mL) at –50 ºC was added XeF_2 (3.5 mg, 2.1×10^{-5} mol, 1.1 equiv). The reaction mixture was stirred at –50 ºC for 45 min, at which time a dark red solution was observed. The reaction mixture was transferred to an NMR tube and frozen. $TMSCF_3$ (8.4 μL, 8.0 mg, 5.6×10^{-5} mol, 3.0 equiv) was added to the NMR tube. The reaction mixture was removed from the dry box and placed in a dry ice / acetone bath, at which temperature the reaction mixture melted resulting in a dark green brown solution. NMR spectra of the reaction mixture were obtained at –80 ºC. The ^{1}H NMR spectrum indicated the presence of TMSF as well as a complex with signals consistent with the structure **9** as drawn above.[x] ^{19}F NMR analysis showed TMSF, which was quantified (40-52%) by integration versus internal standard 1-bromo-4-(trifluoromethyl)benzene.

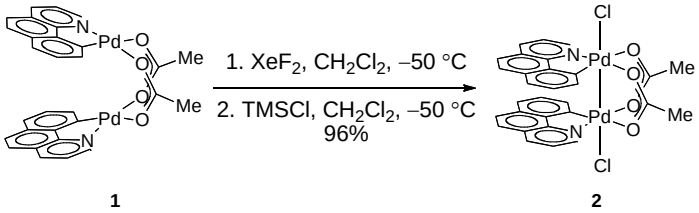
NMR Spectroscopy: ^{1}H NMR (500 MHz, CD_2Cl_2, –80 ºC, δ): 7.85 (br s, 2H), 7.72 (br s, 2H), 7.45–7.44 (m, 4H), 7.32 (br s, 2H), 7.26 (br s, 2H), 7.19–7.14 (m, 2H), 6.85 (br s, 2H), 2.74 (s, 6H).

Discussion of Structure of 9

Thermal instability of **9** has prevented independent characterization of the structure of **9**. The proposed structure of **9** is based on analogy to reactions of **8** with TMSX reagents (X = OAc, Cl), *vide infra*, and based on the similarity of the ^{1}H NMR spectrum of **9** with binuclear Pd(III) complexes **2** and **3**. Below, previously published procedures for the synthesis of **2** and **3**, by treatment of **8** with TMSCl and TMSOAc, respectively, are reproduced.

The acetate chemical shift for **9** is at 2.74 ppm. This is similar to the corresponding chemical shifts of **2** (2.69 ppm) and of **3** (2.71 ppm). By contrast, the corresponding shift in binuclear Pd(II) complex **1** is at 2.38 ppm. The acetate resonances of Pd(IV) complex **5** are at 2.34 and 1.72 ppm, respectively. Thermal instability of **9** prevented the acquisition of ^{13}C NMR and UV-vis spectra as well as mass spectrometric analysis. ^{19}F NMR analysis of the reaction mixture containing proposed structure **9** showed TMSF (δ = –160.3). A single resonance attributable to **9** was not observed.

Benzo[*h*]quinolinyl chloro palladium(III) acetate dimer (2) by Oxidation with XeF_2

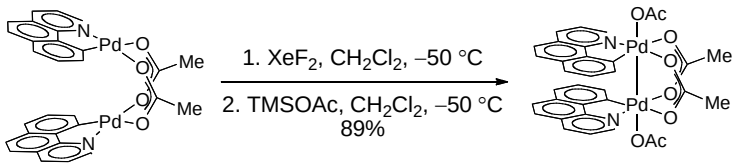


1 **2**

Complex **2** was prepared according to a published procedure.[3] To a solution of benzo[*h*]quinolinyl palladium acetate dimer (**1**) (71.4 mg, 1.04×10^{-4} mol, 1.00 equiv) in CH_2Cl_2 (2.0 mL) at −50 ˚C was added XeF_2 (17.6 mg, 1.04×10^{-4} mol, 1.00 equiv) as a solid in one portion. The color of the solution immediately changed from pale yellow to dark red-brown. After 10 min, TMSCl (27.0 μL, 2.13×10^{-4} mol, 2.05 equiv) was added in one portion. The reaction was stirred for an additional 10 min before solvent was removed in vacuo at −50 ˚C. The residue was triturated with 3 mL Et_2O at −50 ˚C. The residue was dried under vaccuum to afford 75.4 mg of the title compound (96% yield).

^{1}H-NMR (500 MHz, CD_2Cl_2, –50 ºC, δ): 7.71 (br s, 2H), 7.58 (d, J = 7.8 Hz, 2H), 7.45 (dd, J = 7.3 Hz, J = 7.3 Hz, 2H), 7.35 (d, J = 7.8 Hz, 2H), 7.22 (d, J = 8.8 Hz, 2H), 7.18 (d, J = 7.8 Hz, 2H), 7.03 (d, J = 8.3 Hz, 2H), 6.71 (bs, 2H), 2.69 (s, 6H). UV-VIS Spectroscopy (CH_2Cl_2, 0 ˚C): 582 nm ($\varepsilon = 2.99 \times 10^3$ M^{-1} cm^{-1}); 491 nm ($\varepsilon = 7.39 \times 10^3$ M^{-1} cm^{-1}); 417 nm ($\varepsilon = 2.61 \times 10^4$ M^{-1} cm^{-1}); 270 nm ($\varepsilon = 3.69 \times 10^4$ M^{-1} cm^{-1}). These data are in accord with those reported in the literature.[xi]

Benzo[*h*]quinolinyl acetoxy palladium(III) acetate dimer (3) by Oxidation with XeF_2



1 **3**

Complex **3** was prepared according to a published procedure.[3] To a solution of benzo[*h*]quinolinyl palladium acetate dimer (**1**) (61.3 mg, 8.92×10^{-5} mol, 1.00 equiv) in CH_2Cl_2 (2.0mL) was added XeF_2 (15.1 mg, 8.92×10^{-5} mol, 1.00 equiv) at –50 ºC in an N_2-filled dry box. The reaction mixture immediately became dark red. After stirring for 5 min at –50 ºC, TMSOAc (40.1 μL, 2.68×10^{-4} mol, 3.00 equiv) was added in one portion. After 15 min, solvent was removed in vacuo at –50 ºC. The dark red residue was washed with pre-cooled (–50 ºC) Et_2O (2 × 3 mL) and dried at –50 ºC to afford 63.9 mg of the title compound (89% yield) as a 15:1 mixture of isomers (benzoquinolinyl ligand head to tail vs. head to head). The title compound is a moisture sensitive dark red solid.

NMR Spectroscopy: ^{1}H-NMR (500 MHz, CD_2Cl_2, –30 ºC, δ): Head to Tail Isomer: 7.89 (d, *J* = 5.4 Hz, 2H), 7.62 (d, *J* = 7.3 Hz, 2H), 7.47–7.41 (m, 4H), 7.31 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 7.3 Hz, 2H), 7.12 (d, *J* = 8.8 Hz, 2H), 6.71 (dd, *J* = 7.8 Hz, 5.4 Hz, 2H), 2.71 (s, 6H), 1.47 (s, 6H). Head to Head Isomer: 8.26 (d, *J* = 5.2 Hz, 2H), 7.84 (d, 7.8 Hz, 2H), 6.88 (d, *J* = 7.3 Hz, 2H). ^{13}C-NMR (125 MHz, CD_2Cl_2, –30 ºC, δ): Head to Tail Isomer: 187.4, 175.9, 157.4, 150.6, 149.9, 136.8, 136.7, 133.4, 130.4, 127.4, 126.3, 125.6, 124.8, 124.5, 121.2, 25.0, 23.0. UV-VIS Spectroscopy (CH_2Cl_2, 0 ˚C): 419 nm ($\varepsilon = 1.03 \times 10^4$ M^{-1} cm^{-1}); 281 nm ($\varepsilon = 2.48 \times 10^4$ M^{-1} cm^{-1}). These data are in accord with those reported in the literature.[3]

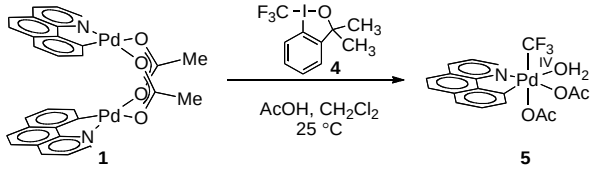
Reaction Kinetics

Initial Rate Kinetics of Oxidation of 1 with 4

The rate-law of oxidation of binuclear Pd(II) complex **1** with **4** to afford mononuclear Pd(IV) complex **5** was determined by examination of the initial rate kinetics of formation of **5** as a function of concentration of each reaction component. This analysis revealed that the rate law is rate = k [**1**] [**4**] [AcOH], consistent with rate-determining oxidation of binuclear Pd complexes to afford a binuclear Pd(III) complex. Experimental details are reported below.

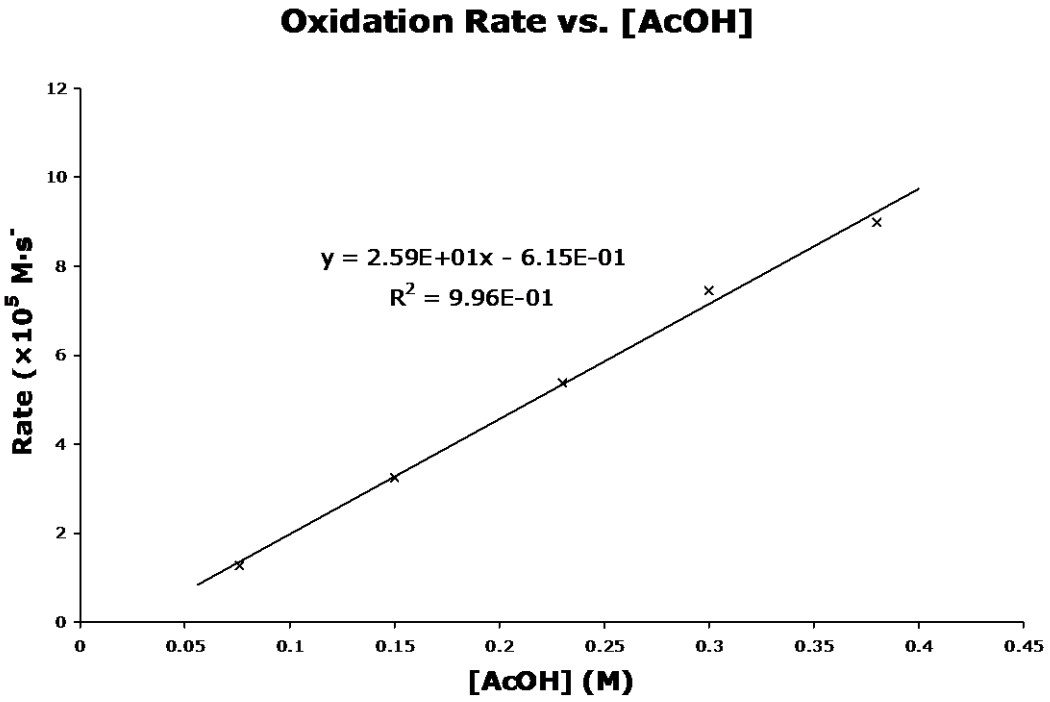
In general, initial rate measurements were carried out as follows. Individual samples were prepared as described below and were inserted into a temperature-controlled NMR spectrometer. The concentration of **5** was assayed by integration of the ^{19}F NMR signal versus the integration of the internal standard signal. For each set of experiments in which the concentration of a reaction component was varied, the initial rate of the fastest reaction (generally, the sample with the highest concentration of the reagent being varied), was determined using a single data point. Examination of the full time course of product formation confirmed that the first data point was representative. The conversion at the first data point in this experiment established the conversion to which subsequent experiments were monitored. Each experimental point is based on a different number of data points, between 1 and 8. We chose to collect data in this way because we were endeavoring to obtain initial rate data at 5-10% yield. To insure that this approach was reproducible, the entire data set used for each of the kinetic order determinations was performed in duplicate.

Reaction order of AcOH in the oxidation of 1 to 5[xii]

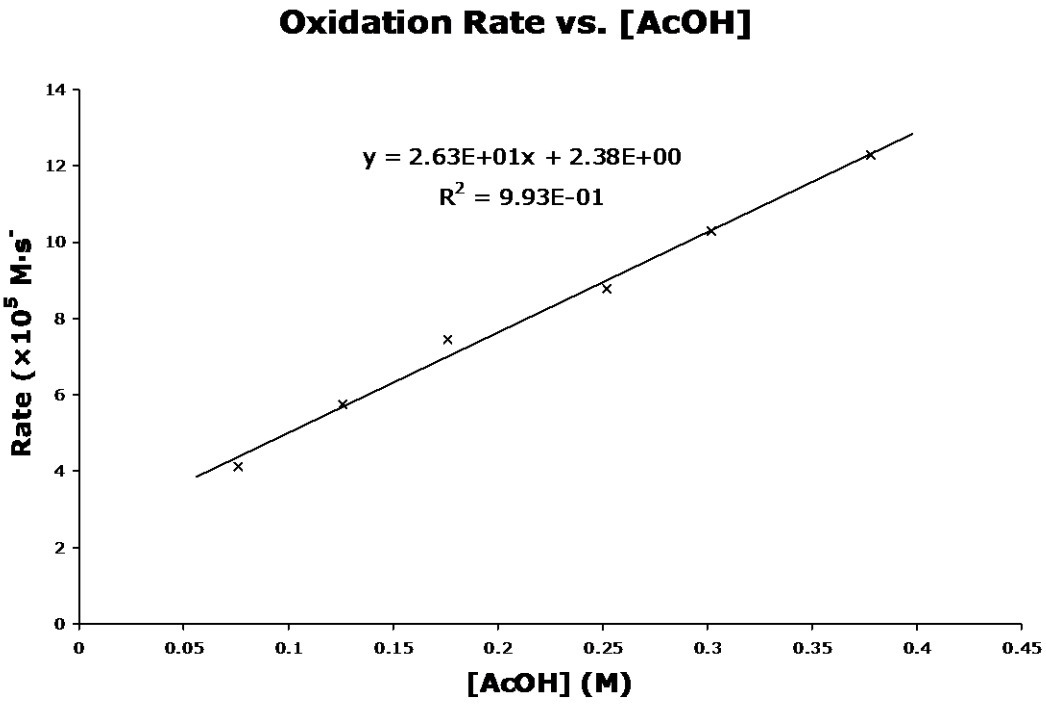


A solution of benzo[*h*]quinolinyl palladium acetate dimer (**1**) (65 mM; 130 mM in Pd) was prepared by dissolving 180 mg of **1** in CH_2Cl_2 (4.0 mL). This solution also contained 200 mM CCl_3F (72 μL). A solution of AcOH in CH_2Cl_2 (4.0 M) was prepared by dissolving AcOH (314 mg, 0.300 mL) in 1.0 mL CH_2Cl_2. A solution of **4** (0.26 M) in CH_2Cl_2 was prepared by dissolving 258 mg of **4** in CH_2Cl_2 (3.0 mL). Samples were prepared with total volumes by combining the following volumes of the above-described solutions (see table below); the solution of **4** was added last. Following addition of **4**, ^{19}F NMR spectra were obtained and the concentration of **5** was quantified by integration of the ^{19}F NMR signal at –25.5 ppm versus the ^{19}F signal of CCl_3F at 1.05 ppm. Initial rates of oxidation were determined from the data obtained.

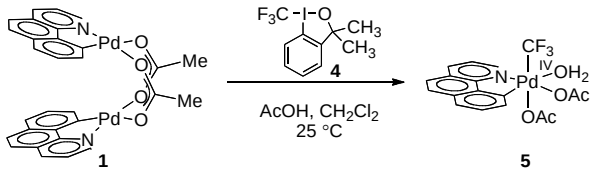
Run	Pd V (μL); C (M)	4 V (μL); C (M)	AcOH V (μL); C (M)	CH_2Cl_2 (V (μL))	**rate** (M/s) (yield (%))
1	400; 0.065	300; 0.098	15; 0.076	85	1.27×10^{-5} (8.6)
2	400; 0.065	300; 0.098	30; 0.15	70	3.25×10^{-5} (14.4)
3	400; 0.065	300; 0.098	45; 0.23	55	5.38×10^{-5} (14.6)
4	400; 0.065	300; 0.098	60; 0.30	40	7.45×10^{-5} (14.2)
5	400; 0.065	300; 0.098	75; 0.38	25	8.99×10^{-5} (14.2)



To evaluate the reliability of the y-intercept on the above plot, a completely independent data set was collected and is plotted below. Based on the close agreement of the slope of the line and the divergent y-intercept, two-term rate laws based on the non-zero intercept are likely not relevant.

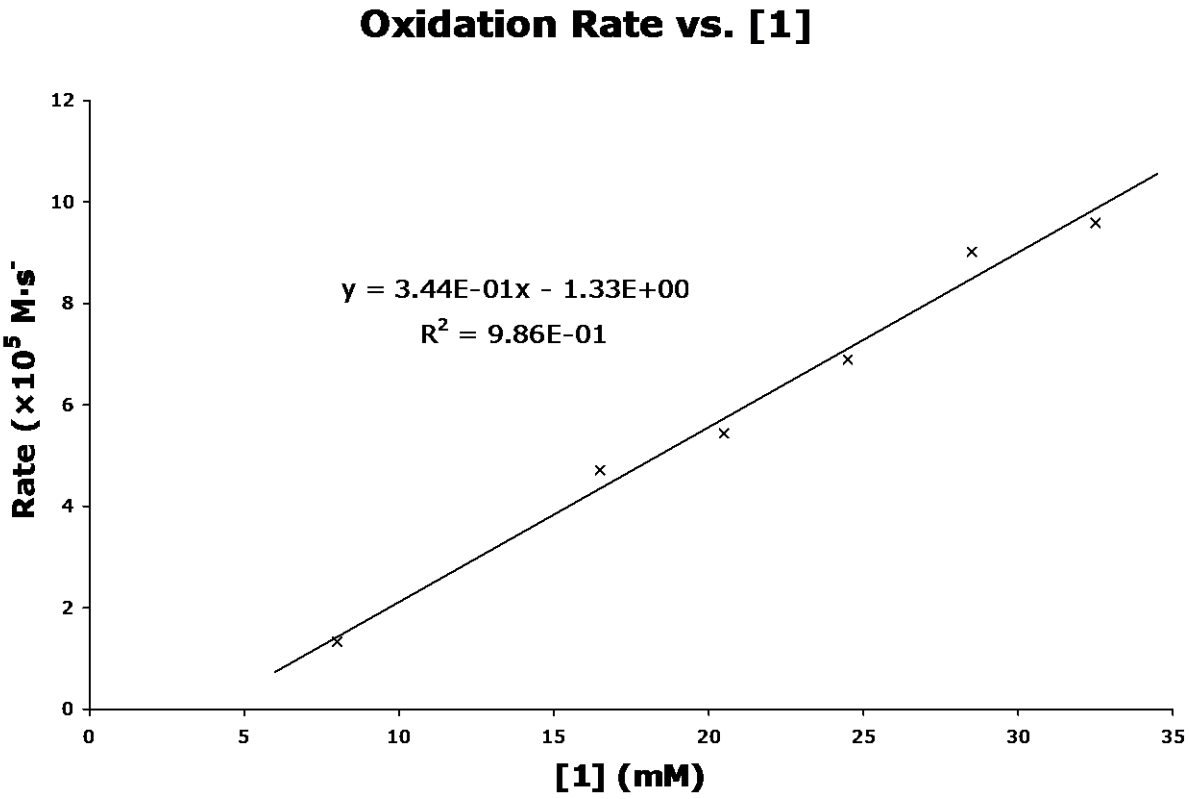


Reaction order of 1 in the oxidation of 1 to 5

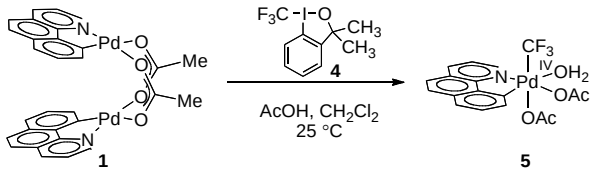


A solution of benzo[*h*]quinolinyl palladium acetate dimer (**1**) (65 mM; 130 mM in Pd) was prepared by dissolving 180 mg of **1** in CH_2Cl_2 (4.0 mL). A solution of AcOH in CH_2Cl_2 (4.0 M) was prepared by dissolving AcOH (314 mg, 0.300 mL) in 1.0 mL CH_2Cl_2. A solution of oxidant (**4**) (0.26 M) in CH_2Cl_2 was prepared by dissolving 258 mg of **4** in CH_2Cl_2 (3.0 mL) and 72 μL CCl_3F. Samples were prepared with total volumes by combining the following volumes of the above-described solutions (see table below); the solution of **4** was added last. Following addition of **4**, ^{19}F NMR spectra were obtained and the concentration of **5** was quantified by integration of the ^{19}F NMR signal at –25.5 ppm versus the ^{19}F signal of CCl_3F at 1.05 ppm. Initial rates of oxidation were determined from the data obtained.

Run	Pd V (μL); C (M)	4 V (μL); C (M)	AcOH V (μL); C (M)	CH_2Cl_2 (V (μL))	**rate** (M/s) (yield (%))
1	100; 0.016	300; 0.098	50; 0.25	350	1.32×10^{-5} (12.4)
2	200; 0.033	300; 0.098	50; 0.25	250	4.71×10^{-5} (7.4)
3	250; 0.041	300; 0.098	50; 0.25	200	5.44×10^{-5} (10.5)
4	300; 0.049	300; 0.098	50; 0.25	150	6.89×10^{-5} (11.8)
5	350; 0.057	300; 0.098	50; 0.25	100	9.02×10^{-5} (15.8)
6	400; 0.065	300; 0.098	50; 0.25	50	9.59×10^{-5} (13.8)



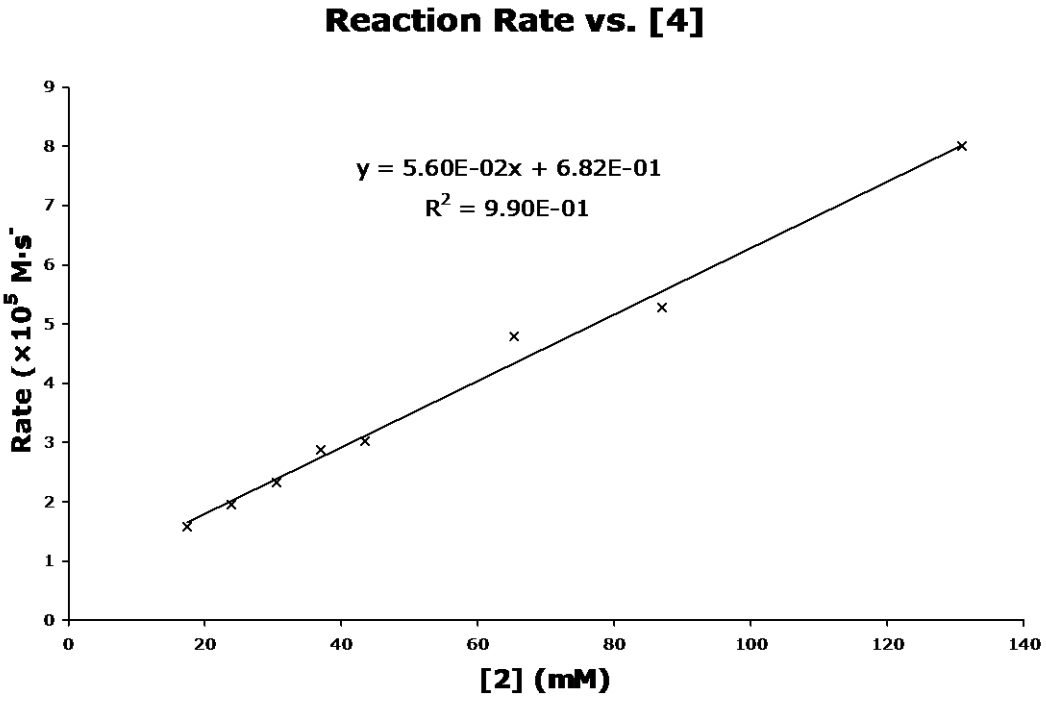
Reaction order of 4 in the oxidation of 1 to 5



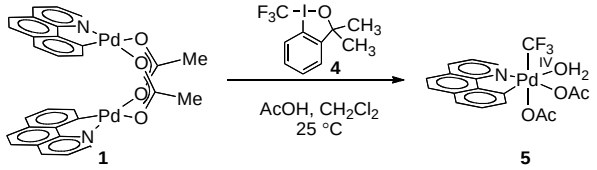
A solution of benzo[*h*]quinolinyl palladium acetate dimer (**1**) (87 mM; 174 mM in Pd) was prepared by dissolving 360 mg of **1** in CH_2Cl_2 (6.0 mL). This solution also contained 200 mM CCl_3F (108 μL). A solution of AcOH in CH_2Cl_2 (4.0 M) was prepared by dissolving AcOH (314 mg, 0.300 mL) in 1.0 mL CH_2Cl_2. A solution of oxidant (**4**) (0.35 M) in CH_2Cl_2 was prepared by dissolving 138 mg of **4** in CH_2Cl_2

(1.2 mL). Samples were prepared with total volumes by combining the following volumes of the above-described solutions (see table below); the solution of **4** was added last. Following addition of **4**, ^{19}F NMR spectra were obtained and the concentration of **5** was quantified by integration of the ^{19}F NMR signal at –25.5 ppm versus the ^{19}F signal of CCl_3F at 1.05 ppm. Initial rates of oxidation were determined from the data obtained.

Run	**Pd** V (μL); C (M)	**4** V (μL); C (M)	**AcOH** V (μL); C (M)	**CH_2Cl_2** (V (μL))	**rate** (M/s) (yield (%))
1	400; 0.087	40; 0.017	30; 0.15	330	1.58×10^{-5} (7.9)
2	400; 0.087	55; 0.024	30; 0.15	315	1.96×10^{-5} (7.9)
3	400; 0.087	70; 0.031	30; 0.15	300	2.33×10^{-5} (7.4)
4	400; 0.087	85; 0.037	30; 0.15	285	2.88×10^{-5} (7.0)
5	400; 0.087	100; 0.044	30; 0.15	270	3.03×10^{-5} (7.3)
6	400; 0.087	150; 0.065	30; 0.15	220	4.79×10^{-5} (8.5)
7	400; 0.087	200; 0.087	30; 0.15	170	5.28×10^{-5} (6.7)
8	400; 0.087	300; 0.13	30; 0.15	70	8.01×10^{-5} (6.9)



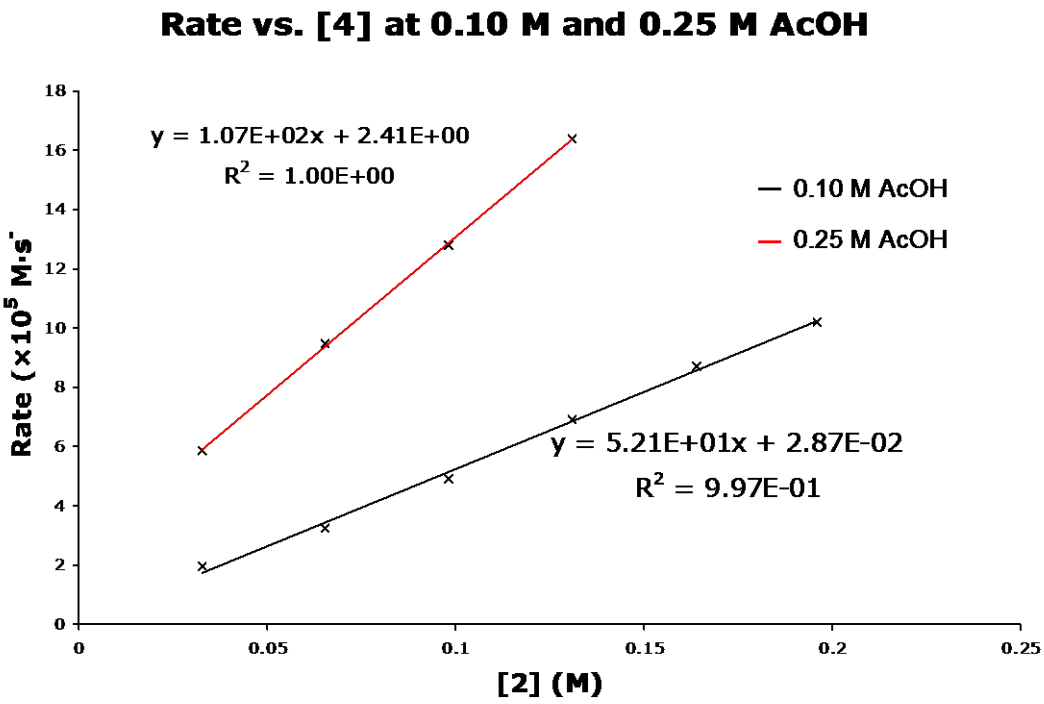
Rate of Oxidation of 1 as a function of [4] at two concentrations of AcOH



To confirm the results reported regarding the reaction order of both AcOH and oxidant, the following experiment was carried out in which the rate dependence on oxidant (**4**) was determined at two concentrations of AcOH.

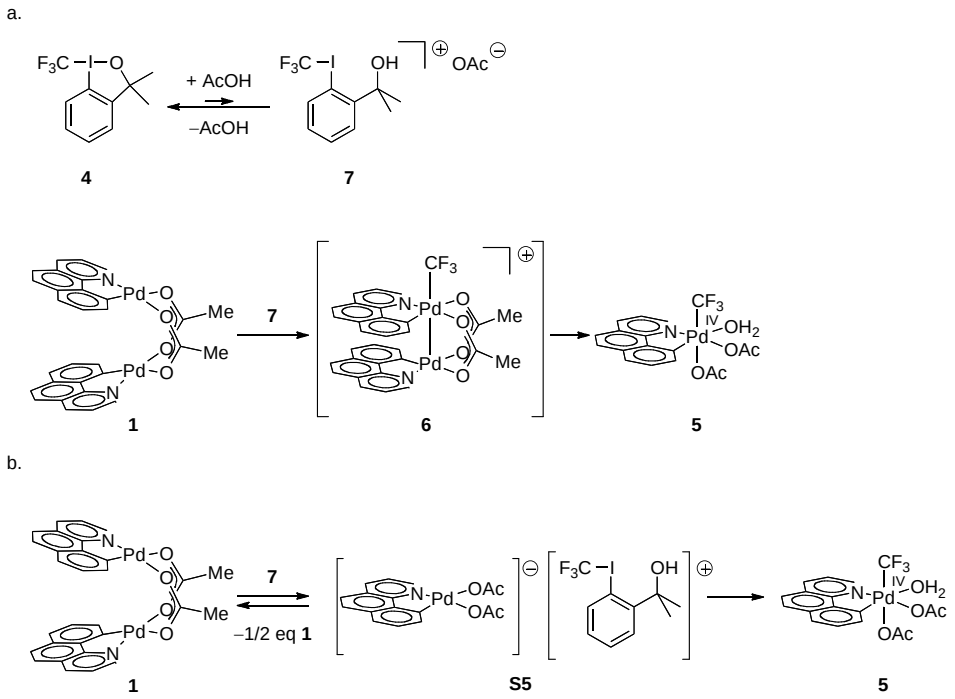
A solution of benzo[*h*]quinolinyl palladium acetate dimer (**1**) (65 mM; 130 mM in Pd) was prepared by dissolving 252 mg of **1** in CH_2Cl_2 (5.6 mL). This solution also contained 200 mM CCl_3F (100 μL). A solution of AcOH in CH_2Cl_2 (4.0 M) was prepared by dissolving AcOH (314 mg, 0.300 mL) in 1.0 mL CH_2Cl_2. A solution of oxidant (**4**) (0.52 M) in CH_2Cl_2 was prepared by dissolving 414 mg of **4** in CH_2Cl_2 (2.4 mL). Samples were prepared with total volumes by combining the following volumes of the above-described solutions (see table below); the solution of **4** was added last. Following addition of **4**, ^{19}F NMR spectra were obtained and the concentration of **5** was quantified by integration of the ^{19}F NMR signal at –25.5 ppm versus the ^{19}F signal of CCl_3F at 1.05 ppm. Initial rates of oxidation were determined from the data obtained.

Run	**Pd** V (μL); C (M)	**4** V (μL); C (M)	**AcOH** V (μL); C (M)	**CH_2Cl_2** (V (μL))	**rate** (M/s) (yield (%))
1	400; 0.087	50; 0.033	20; 0.10	330	1.96×10^{-5} (10.6)
2	400; 0.087	100; 0.065	20; 0.10	280	3.25×10^{-5} (11.1)
3	400; 0.087	150; 0.098	20; 0.10	230	4.91×10^{-5} (8.3)
4	400; 0.087	200; 0.13	20; 0.10	180	6.92×10^{-5} (8.6)
5	400; 0.087	250; 0.16	20; 0.10	130	8.73×10^{-5} (7.6)
6	400; 0.087	300; 0.20	20; 0.10	80	1.02×10^{-4} (8.9)
7	400; 0.087	50; 0.033	50; 0.25	300	5.86×10^{-5} (11.3)
8	400; 0.087	100; 0.065	50; 0.25	250	9.48×10^{-5} (11.0)
9	400; 0.087	150; 0.098	50; 0.25	200	1.28×10^{-4} (9.3)
10	400; 0.087	200; 0.13	50; 0.25	150	1.64×10^{-4} (8.1)

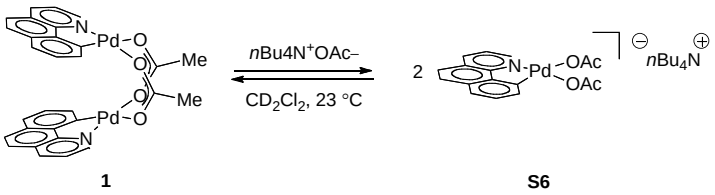


Discussion of Potential Oxidation Pathways via Mononuclear Pd Complexes

The experimentally derived rate law is: rate = *k* [**1**] [**4**] [AcOH]. This rate law is consistent with pre-equilibrium protonation of **4** by acetic acid followed by oxidation of binuclear Pd(II) complex **1** (a, scheme below). This rate law is also consistent with pre-equilibrium association of the acetate counterion of **7** participating in bridge-splitting equilibrium with binuclear Pd(II) complex **1** to afford mononuclear Pd(II) palladate complex **S5**, which undergoes subsequent oxidation to afford the observed mononuclear Pd(IV) complex **5**. While we can not differentiate between these two possibilities by reaction kinetics analysis, below are outlined a series of experiments that we carried out which suggest that a mononuclear complex is not required for oxidation. First, we showed that acetate ions can bind to the Pd(II) centers of **1** by treating **1** with *n*-Bu_4NOAc to afford **S6**. We next prepared a protonated derivative of Togni reagent (**S7**) bearing a weakly coordinating couterion by treating **4** with CSA. Finally, we have shown that oxidation of **1** to **5** proceeds in the absence of exogenous anions to promote monomerization of **1**; oxidation of **1** with **S7** affords mononuclear Pd(IV) complex **5** in 36% yield (based on Pd). The reaction of **1** with **S7** suggests that an anionic donor to monomerize **1** is not required for oxidation to afford **5**.



Benzo[*h*]quinolinyl *bis*-acetato palladate (S6)

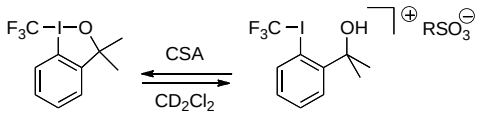


To benzo[*h*]quinolinyl palladium acetate dimer (**1**) (2.7 mg, 3.9 μmol, 1.0 equiv) in CD_2Cl_2 (0.50 mL) at 23 ºC was added *n*-Bu_4NOAc (2.8 mg, 9.4 μmol, 2.4 equiv). After 10 min, a ^1H NMR spectrum was obtained. The spectrum contained both signals attributable to **1** as well as signals attributable to a new species, assigned as **S6**. The assignment of **S6** as a monomer is based primarily on the large downfield shift of the benzo[*h*]quinolinyl protons that is observed.

The concentration of **S6** was found to be dependent on the concentration of *n*-Bu_4NOAc added. Above, at 19 mM *n*-Bu_4NOAc (2.4 equiv), a ratio of 84 : 16 (**1** : **S6**) was observed. In a second experiment, at 190 mM *n*-Bu_4NOAc (24 equiv), a ratio of 14 : 86 (**1** : **S6**) was observed. The ^1H NMR spectra of these two conditions are reproduced in the 'NMR Data' section.

NMR Spectroscopy: ^1H NMR (500 MHz, CD_2Cl_2, 23 ºC, δ): 8.67 (d, *J* = 5.4, 1H), 8.25 (d, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 8.5 Hz, 1H), 7.56 (d, J = 8.5 Hz, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.41 (dd, J = 8.5 Hz, 5.4 Hz, 1H), 7.36–7.33 (m, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 2.07 (s, 3H).

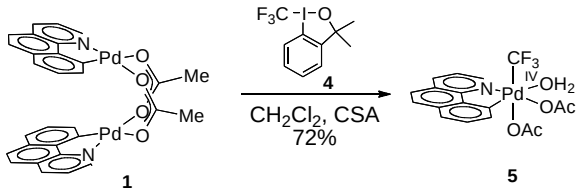
Protonation of 4 with CSA



To 1-trifluoromethyl-1,3-dihydro-3,3-dimethyl-1,2-benziodoxole (**4**) (38 mg, 0.12 mmol, 1.0 equiv) in CD_2Cl_2 (0.60 mL) at 23 ºC was added CSA (27 mg, 0.12 mmol, 1.0 equiv) in one portion. ^1H and ^{19}F NMR spectra were obtained which showed the disappearance of the signals attributable to **4** and the appearance of a new set of signals, assigned to **S7**. Stacked ^1H and ^{19}F NMR spectra of **4** and **S7** are reproduced in the 'NMR Data' section.

NMR Spectroscopy: ^1H NMR (400 MHz, CD_2Cl_2, 23 ºC, δ): 7.69–7.63 (m, 2H), 7.57–7.50 (m, 2H), 1.70 (s, 6H). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –26.0.

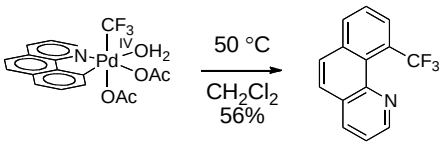
Benzo[*h*]quinolinyl trifluromethyl palladium(IV) diacetate aquo complex (5)



To benzo[*h*]quinolinyl palladium acetate dimer (**1**) (10 mg, 0.015 mmol, 1.0 equiv) in CD_2Cl_2 (0.60 mL) in a J. Young NMR tube at 23 ºC was added CSA (27 mg, 0.12 mmol, 8.0 equiv) and 1-trifluoromethyl-1,3-dihydro-3,3-dimethyl-1,2-benziodoxole (**4**) (38 mg, 0.12 mmol, 8.0 equiv), sequentially. The homogeneous reaction mixture was kept at 23 ºC for 11 h and fluorobenzene (2.0 μL, 2.1 mg) was added to the reaction before a ^1H and ^{19}F NMR spectra were obtained. The yield for **5** (36% based on Pd) was determined by comparing the integration of the ^{19}F NMR resonance of **5** and that of fluorobenzene (–113.2 ppm). In addtion to compound **5**, 10-(trifluoromethyl)benzo[*h*]quinoline (**S8**) was observed (36% yield, based on Pd).

Spectral data for compound **5** prepared by this procedure are identical to those reported above. Spectral data for **S8** prepared by this procedure are identical to those reported in the literature and correspond to those obtained from an authentic sample (see below).

10-(trifluoromethyl)benzo[*h*]quinoline (S8)



5 **S8**

A solution of benzo[*h*]quinolinyl trifluromethyl palladium(IV) diacetate aquo complex (**5**) (220 mg, 0.449 mmol, 1.00 equiv) in CH_2Cl_2 was heated to 50 ºC. After 12 h, solvent was removed in vacuo and the residue was purified by chromatography on SiO_2 gel eluting with EtOAc / hexanes (1 : 4 (v/v)) to afford 62.2 mg of the title compound as a colorless solid (56% yield).

R_f = 0.51 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 9.07 (dd, *J* = 4.2 Hz, 1.9 Hz, 1H), 8.25 (d, *J* = 7.6 Hz, 1H), 8.20 (dd, *J* = 8.1 Hz, 1.9 Hz, 1H), 8.11 (d, *J* = 7.6 Hz, 1H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.78 (d, *J* = 8.6 Hz, 1H), 7.74 (dd, *J* = 8.2 Hz, 8.2 Hz, 1H), 7.57 (dd, *J* = 8.1 Hz, 4.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, 23 ºC, δ): 147.8, 145.13, 135.5, 135.4, 132.9, 128.1 (q, *J* = 8.0 Hz), 128.0, 127.7, 126.9, 126.7, 122.1. ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –57.2. These spectroscopic data correspond to those reported in the literature.[xiii]

X-ray Crystallographic Analysis

Complex **1** has been crystallized by vapor diffusion of pentane into a concentrated CH_2Cl_2 solution of **1**. Two crystal morphologies have been obtained: needle-like and prismatic crystals have been observed. The structure of the needle-shaped crystals has previously been reported[9] and has been deposited in the Cambridge Crystal Structure Database as CCDC 705005. The structure of the prismatic morphology of **1** is reported here for the first time and has been deposited in the Cambridge Crystal Structure Database as CCDC 832191. Experimental data is included below.

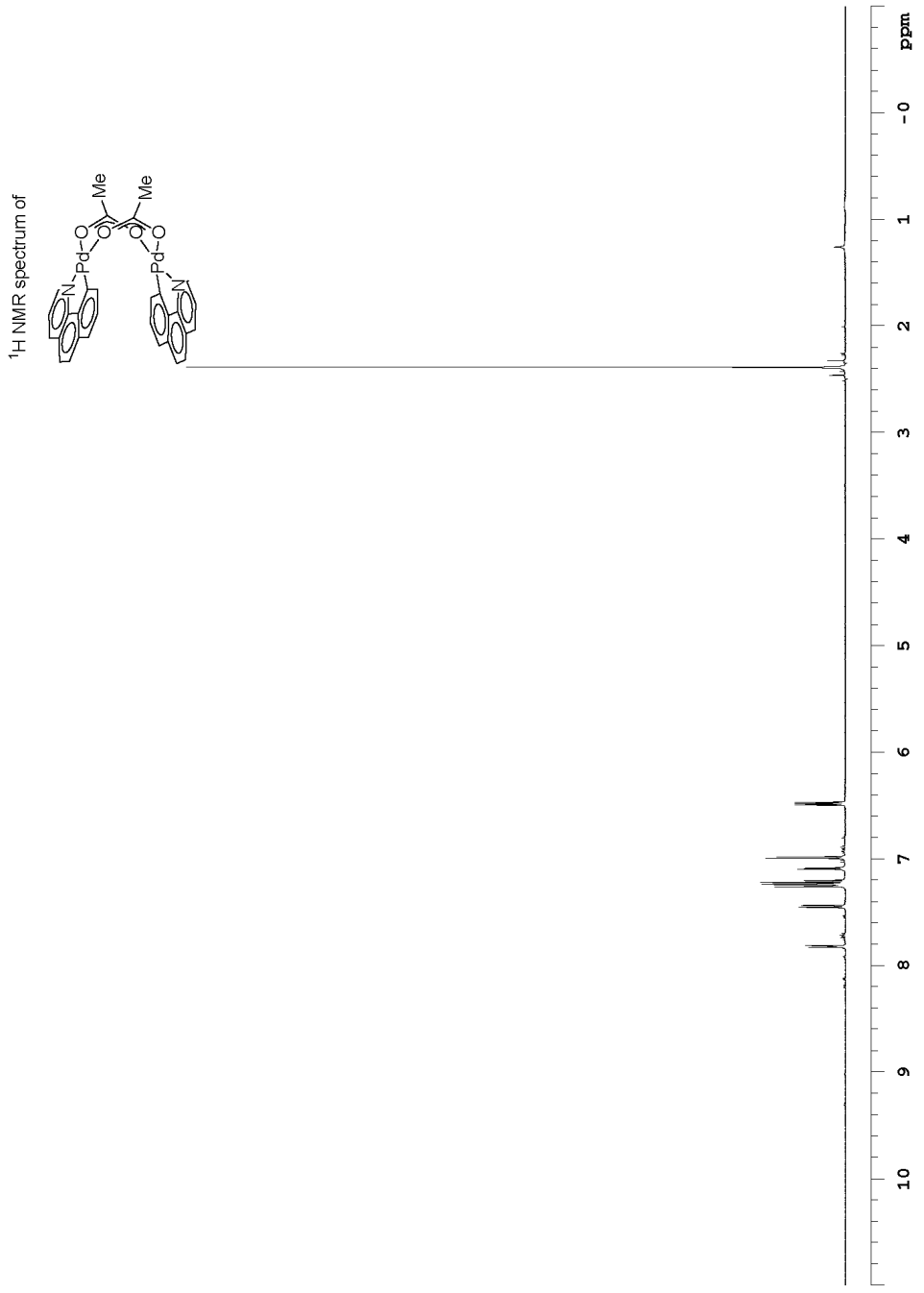
Benzo[*h*]quinolinyl Palladium Acetate Dimer (1) (Prismatic Morphology) (CCDC 832191)

An orange prismatic crystal suitable for x-ray diffraction was obtained by vapor diffusion of pentane into a saturated CH_2Cl_2 solution of **1**. Data was collected on a crystal mounted on a diffractometer at 100 K. The intensities of the reflections were collected by means of a Bruker APEX II CCD diffractometer (MoK radiation, =0.71073 Å), and equipped with an Oxford Cryosystems nitrogen flow apparatus. The collection method involved 0.5 scans in at 28 in 2. Data integration down to 0.82 Å resolution was carried out using SAINT V7.46 A (Bruker diffractometer, 2009) with reflection spot size optimisation. Absorption corrections were made with the program TWINABS. The structure was solved by the direct methods procedure and refined by least-squares methods again F2 using SHELXS-97 and SHELXL-97 (Sheldrick, 2008). Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were allowed to ride on the respective atoms. Crystal data as well as details of data collection and refinement are summarized in Table 1 and geometric parameters are shown in Table 2.

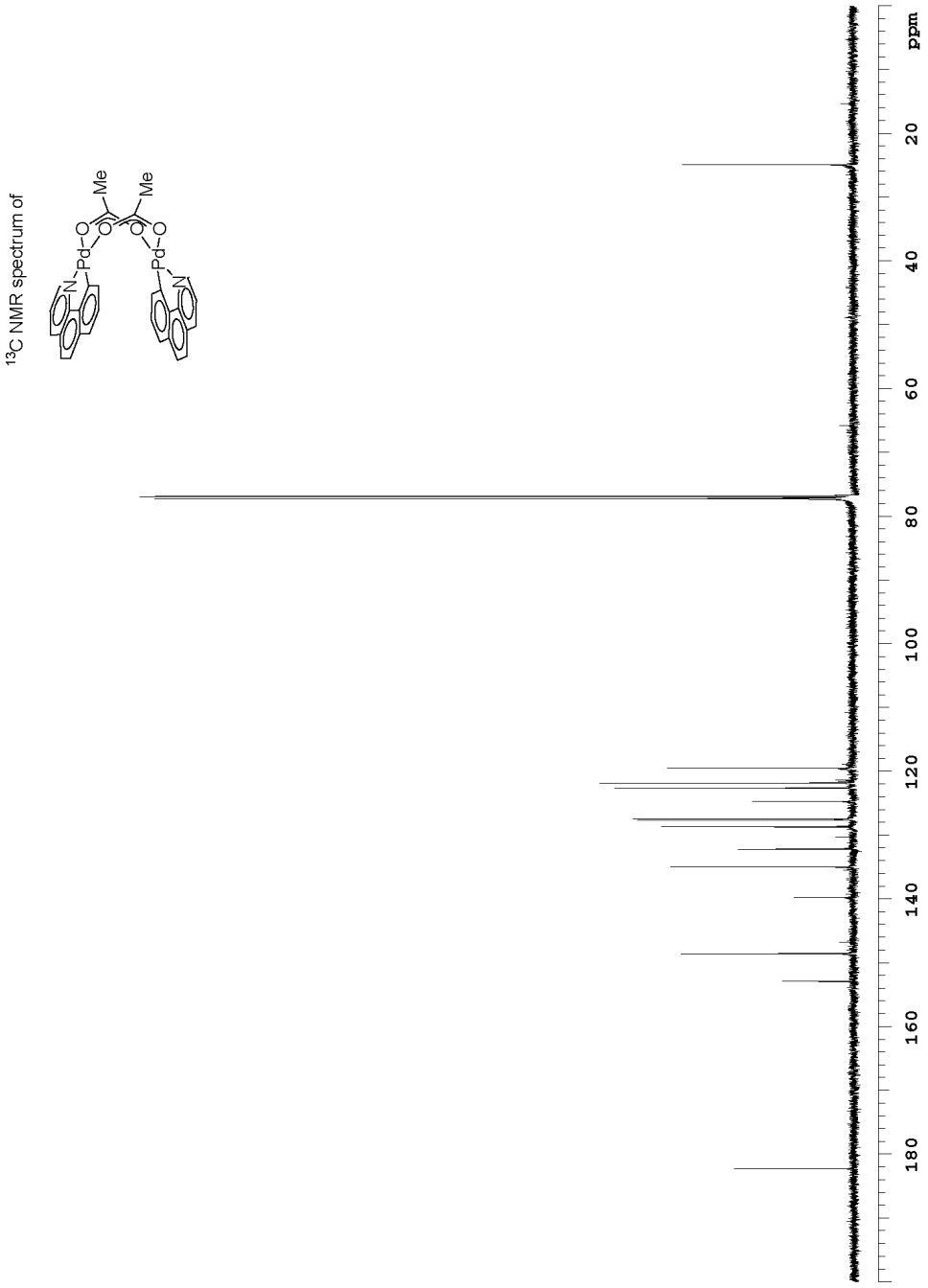
Table 1. Experimental details

Identification Code	**1** (CCDC 832191)
Chemical formula	$C_{184}H_{140}Cl_8N_{12}O_{24}Pd_{12}$
M_r	4463.48
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	100
a, *b*, *c* (Å)	17.1241 (6), 20.2806 (7), 23.2979 (9)
a, b, g (°)	89.559 (2), 89.230 (2), 88.773 (2)
V (Å^3)	8088.3 (5)
Z	2
Radiation type	Mo *K*a
m (mm^{-1})	1.51
Crystal size (mm)	0.20 × 0.14 × 0.12
Data collection	
Absorption correction	Multi-scan TWINABS
T_{min}, T_{max}	0.753, 0.840
No. of measured, independent and observed [I > 2s(I)] reflections	60924, 60924, 45721
R_{int}	0.0000
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.048, 0.107, 1.04
No. of reflections	60924
No. of parameters	2178
No. of restraints	1
H-atom treatment	H-atom parameters constrained
D⟩$_{max}$, D⟩$_{min}$ (e Å^{-3})	1.39, -1.03

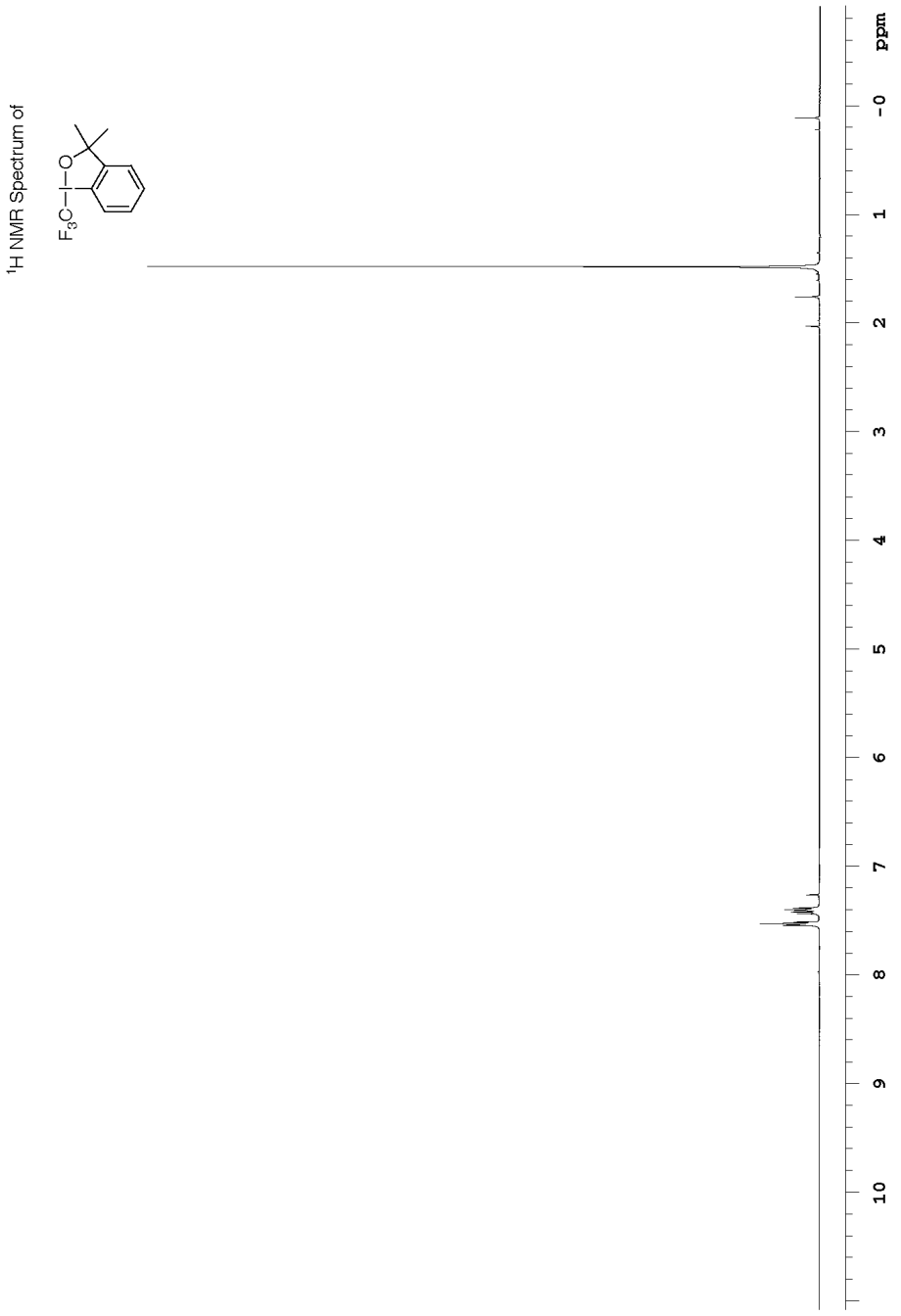
NMR Data



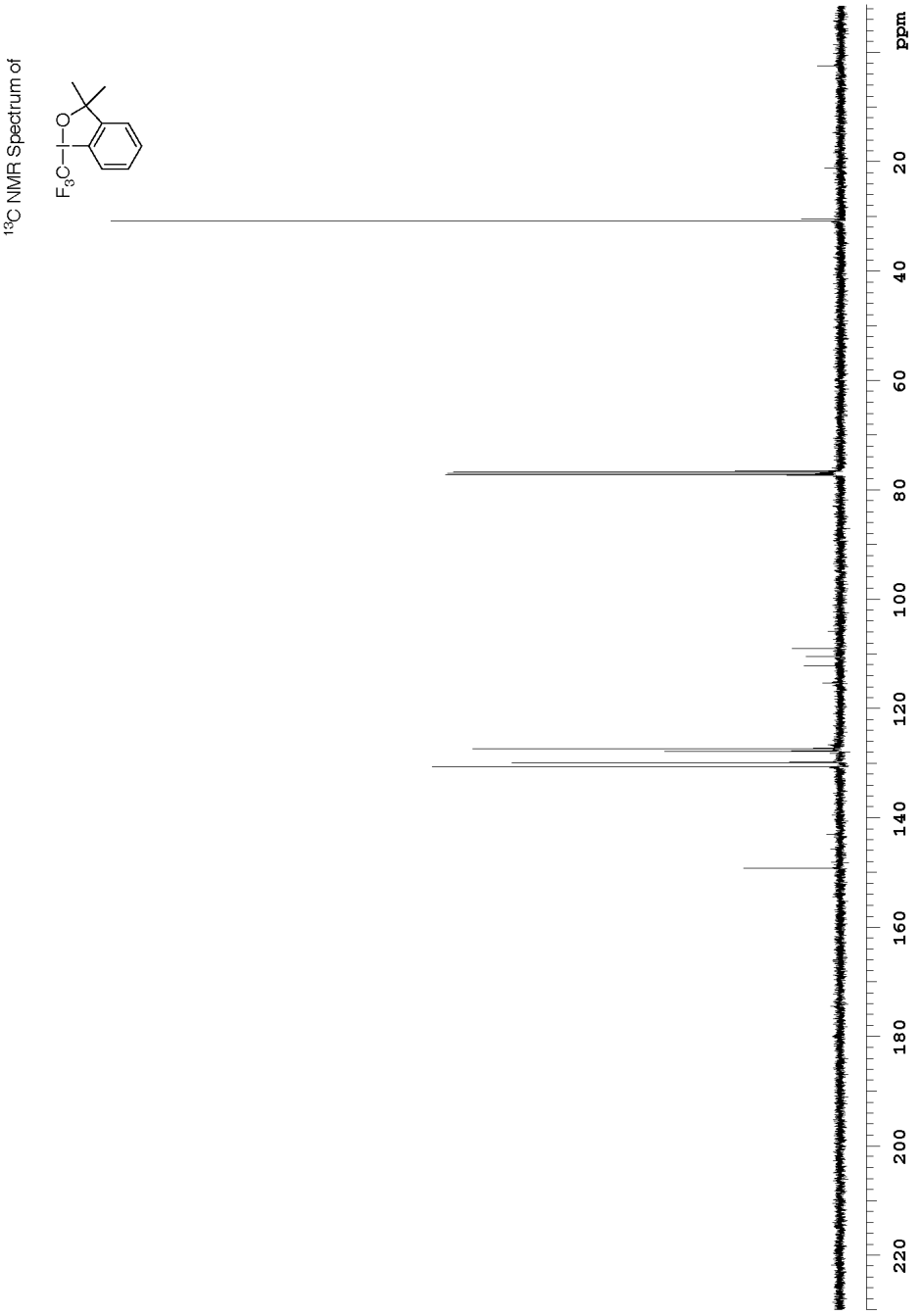
^{1}H NMR spectrum of **1** in $CDCl_3$ at 23 °C.



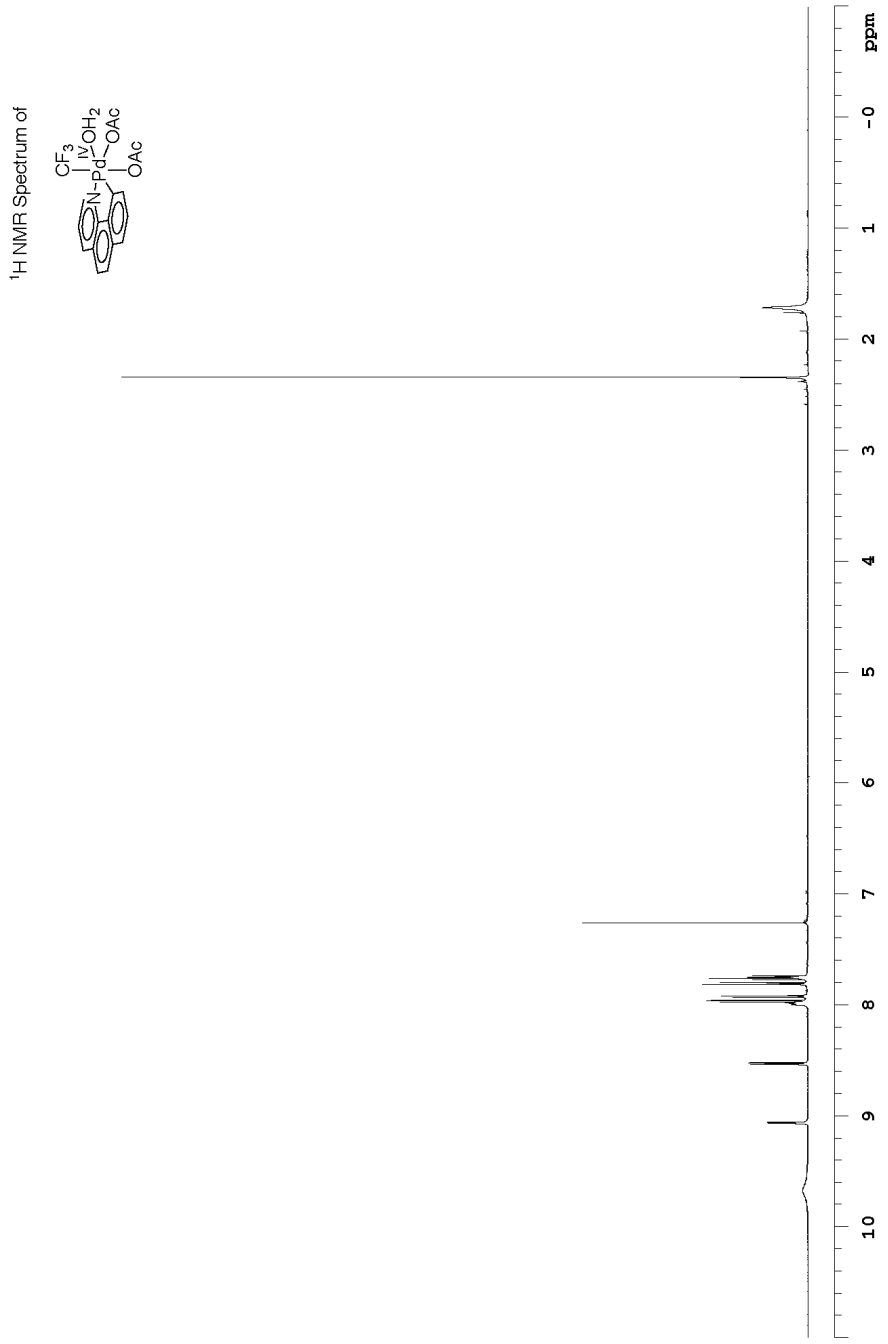
^{13}C NMR spectrum of **1** in $CDCl_3$ at 23 °C.



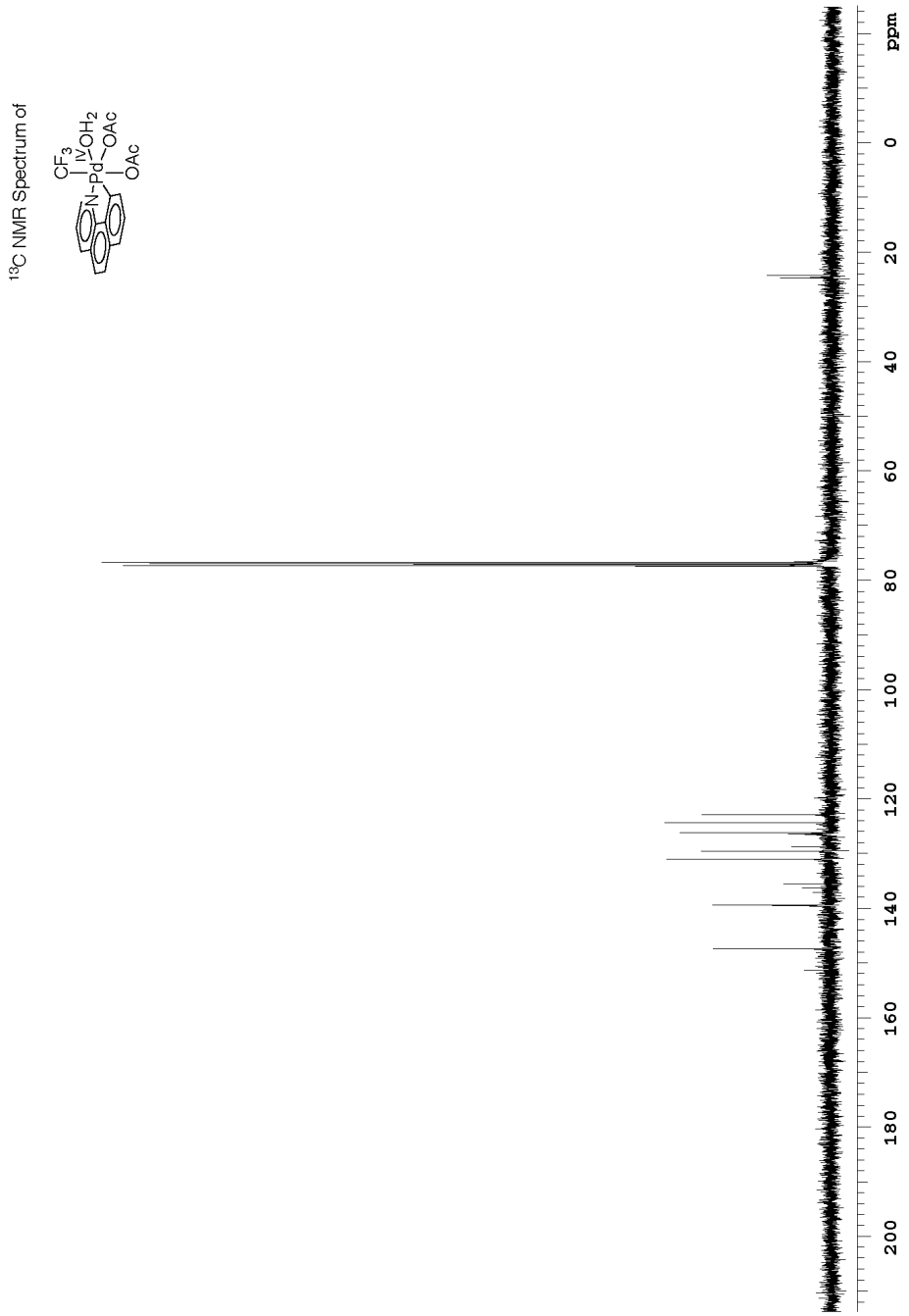
^{1}H NMR spectrum of **4** in $CDCl_3$ at 23 °C.



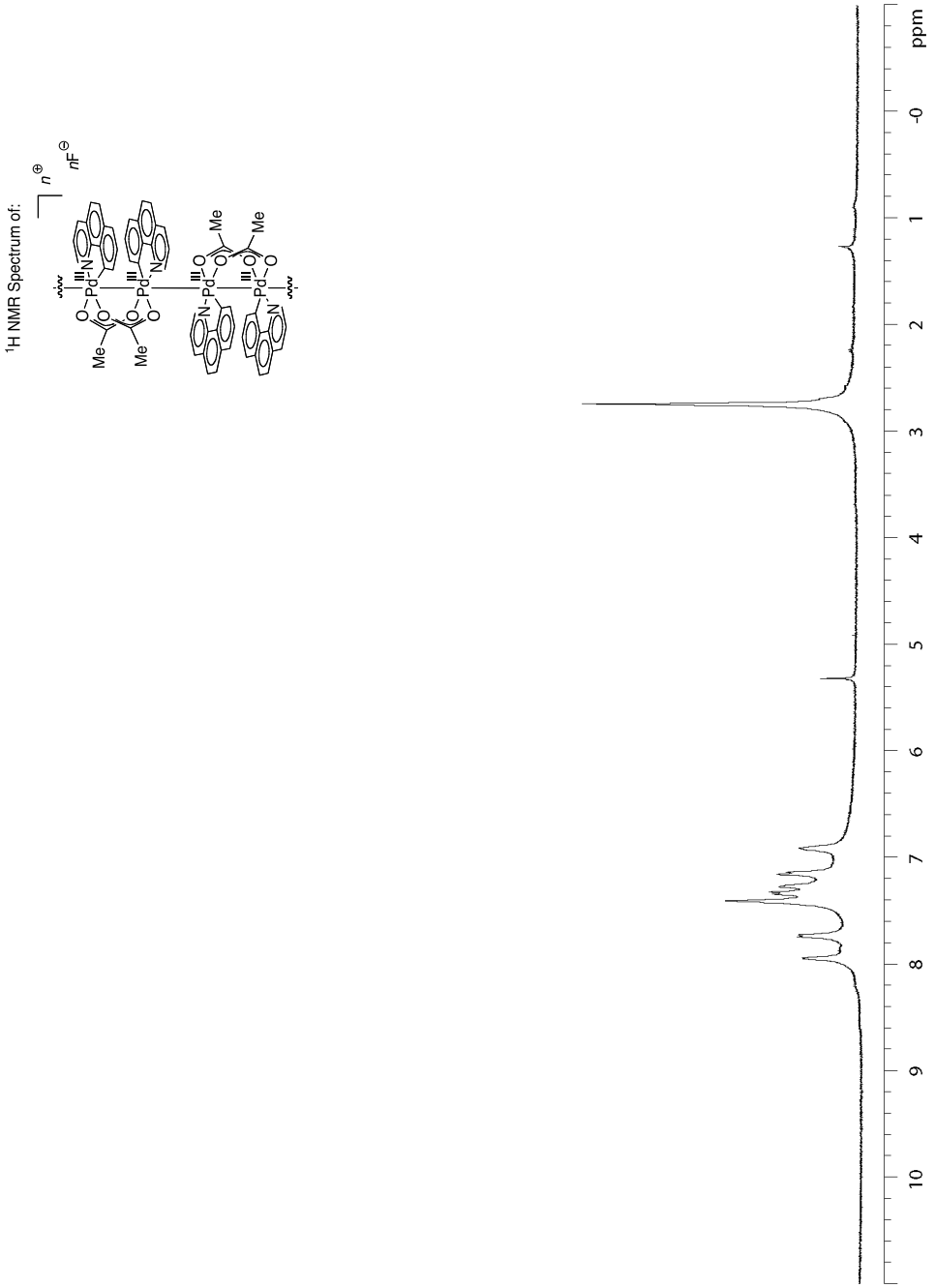
^{13}C NMR spectrum of **4** in $CDCl_3$ at 23 °C.



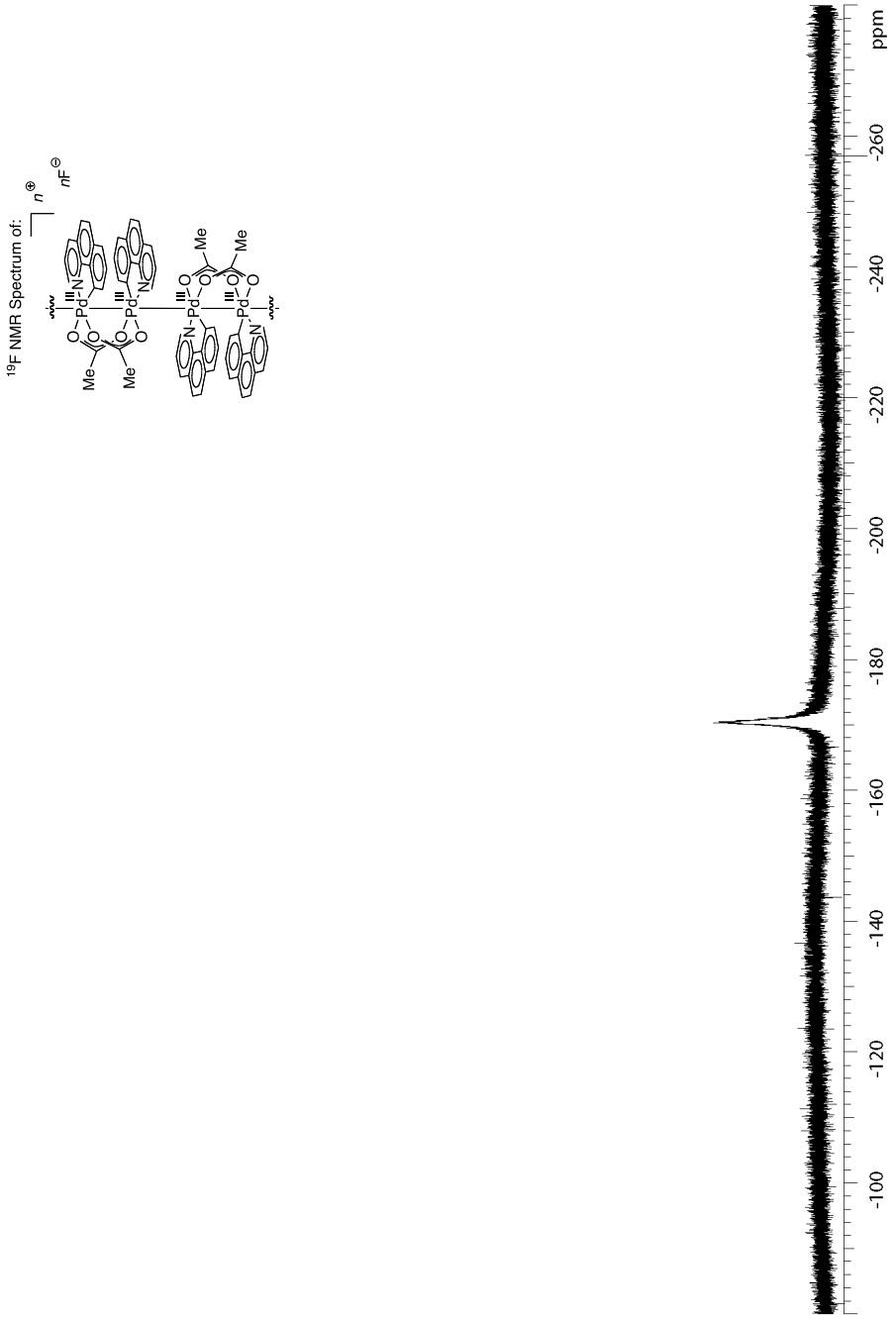
^{1}H NMR spectrum of **5** in $CDCl_3$ at 23 °C.



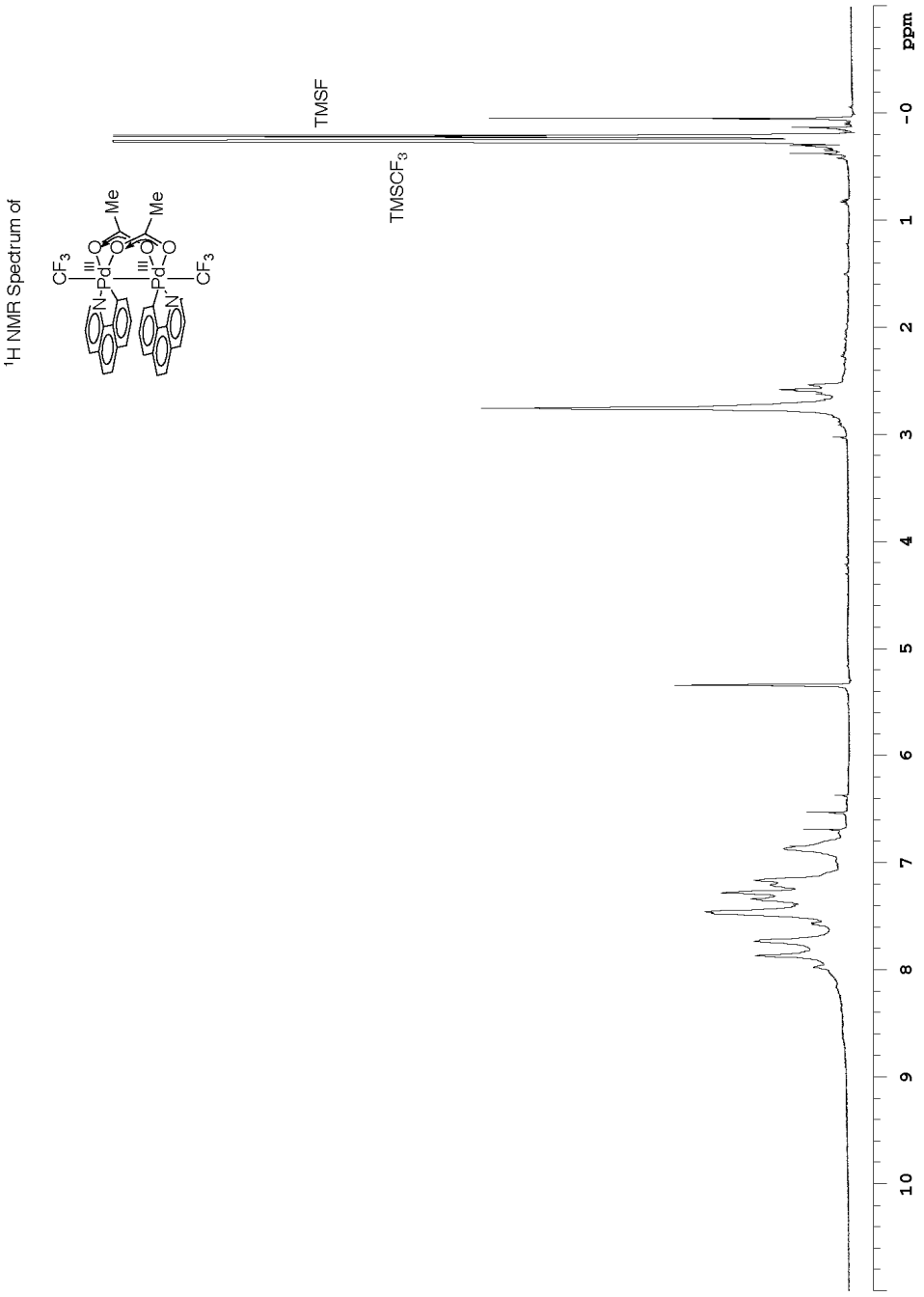
^{13}C NMR spectrum of **5** in $CDCl_3$ at 23 °C.



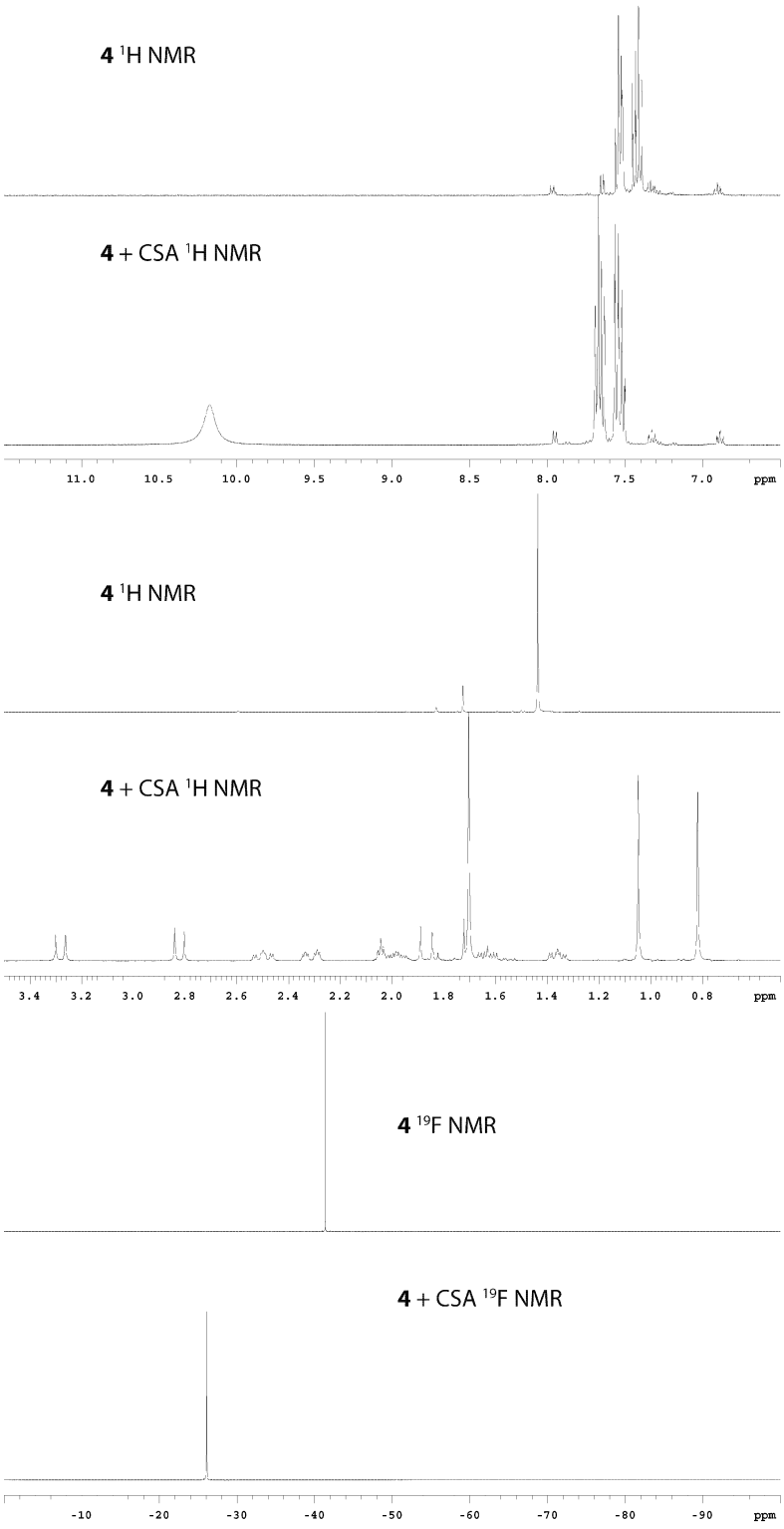
^{1}H NMR of **8** in CD_2Cl_2 at −10 °C

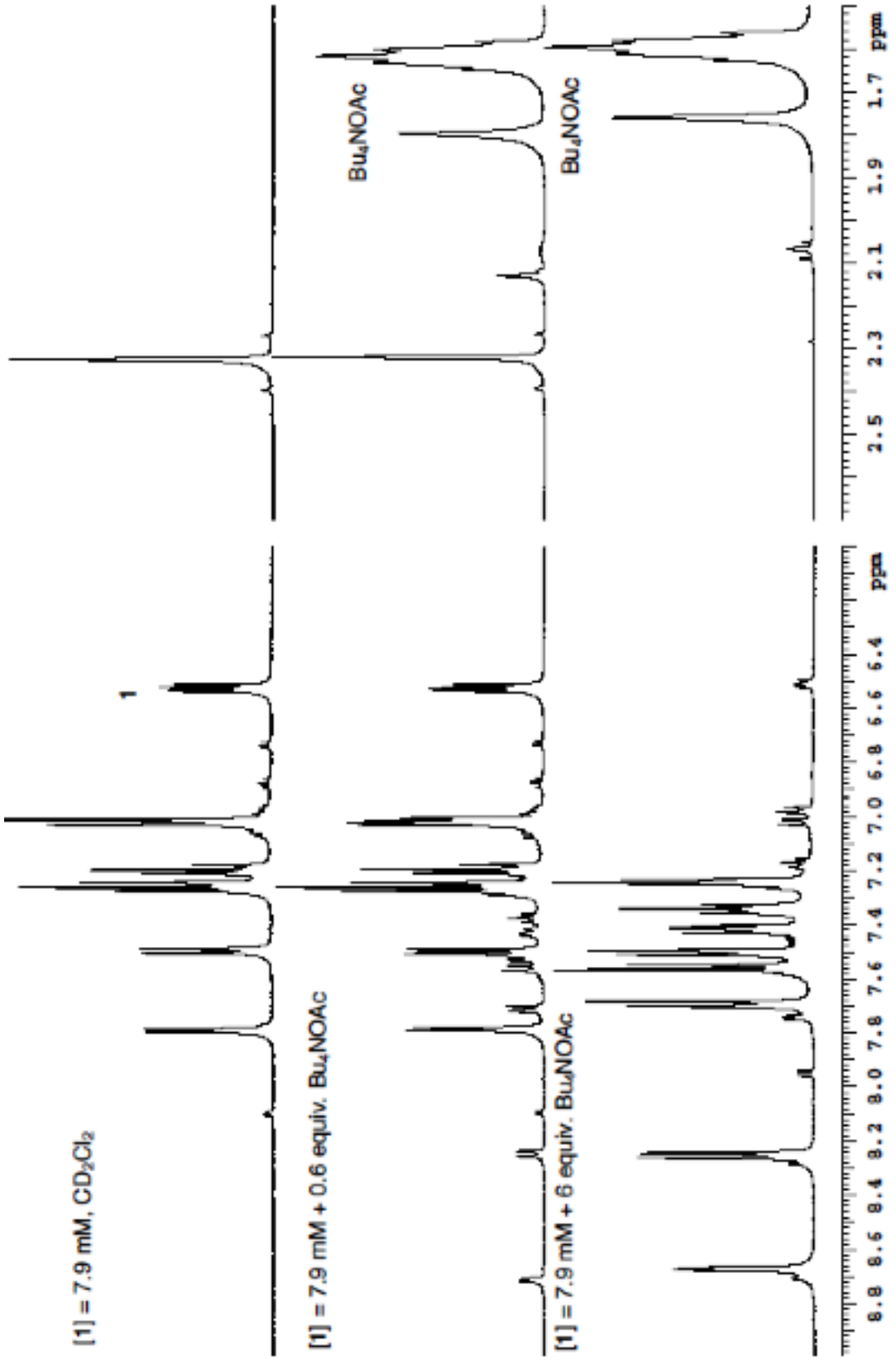


^{19}F NMR of **8** in CD_2Cl_2 at –10 °C



^{1}H NMR spectrum of **9** in CD_2Cl_2 at –80 °C.


4 1H NMR
4 + CSA 1H NMR
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
ppm
4 1H NMR
4 + CSA 1H NMR
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
ppm
4 19F NMR
4 + CSA 19F NMR
-10
-20
-30
-40
-50
-60
-70
-80
-90
ppm


[1] = 7.9 mM, CD_2Cl_2
1
[1] = 7.9 mM + 0.6 equiv. Bu_4NOAc
Bu_4NOAc
[1] = 7.9 mM + 6 equiv. Bu_4NOAc
Bu_4NOAc
8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 ppm
2.5 2.3 2.1 1.9 1.7 ppm

Computational Results

Cartesian coordinates and electronic energies (E), enthalpies (H) and Gibbs free energies for all of the calculated structures

Structure A

(optimized by M06/BS1)

E (BS1) = -2156.72570336 au

H (BS1) = -2156.220911 au

G(BS1) = -2156.326051 au

E(M06/BS2//M06/BS1, Solvent = CH_2Cl_2) = -2159.70179856 au

E(BP86/BS2//M06/BS1, Solvent = CH_2Cl_2) = -2161.14718805 au

E(TPSS/BS2//M06/BS1, Solvent = CH_2Cl_2) = -2161.15063087 au

E(wB97XD/BS2//M06/BS1, Solvent = CH_2Cl_2) = -2160.33723973 au

Pd	-0.468393	-1.279002	-1.459351
Pd	-1.463970	0.296426	0.559093
N	1.126257	-0.067933	-1.954114
N	0.230968	0.066013	1.704602
C	1.123527	1.011542	-2.726322
C	0.536028	-0.950043	2.502281
H	0.177173	1.256838	-3.206511
H	-0.236588	-1.702191	2.649930
C	2.278709	1.787058	-2.897953
C	1.796956	-1.029720	3.106888
H	2.017789	-1.871786	3.756800
C	3.444363	1.427250	-2.248868
C	2.740613	-0.051952	2.855713
H	4.349542	2.022958	-2.365979
H	3.729346	-0.110681	3.310378
C	3.472001	0.274955	-1.441735
C	2.428196	1.028169	2.010628
C	4.617358	-0.221455	-0.736608
C	3.311429	2.106494	1.676961
H	5.551474	0.334744	-0.807808
H	4.319279	2.095533	2.090003
C	4.554242	-1.379628	-0.019604
C	2.901812	3.130547	0.876124
H	5.444064	-1.755035	0.485882
H	3.582115	3.950975	0.649050
C	3.342370	-2.143194	0.077738
C	1.579406	3.169624	0.318785
C	3.218192	-3.359237	0.778524
C	1.086090	4.203160	-0.503236
H	4.088668	-3.781098	1.280149
H	1.726644	5.052748	-0.736923
C	2.006580	-4.023518	0.804051
C	-0.204622	4.151484	-0.992178
H	1.929397	-4.976361	1.325761
H	-0.579523	4.968591	-1.606043
C	0.857928	-3.502787	0.166384

C	-1.064995	3.063896	-0.714250
H	-0.077293	-4.060408	0.200029
H	-2.082009	3.060154	-1.102385
C	0.946649	-2.304294	-0.510086
C	-0.583685	2.039534	0.062233
C	2.192735	-1.643439	-0.568045
C	0.711591	2.096539	0.605802
C	2.273948	-0.450189	-1.329122
C	1.137672	1.048385	1.457888
O	-1.925173	-2.594855	-0.873738
O	-3.066574	0.630315	-0.650085
O	-2.253107	-1.647045	1.142199
O	-1.955821	-0.057813	-2.488409
C	-2.449606	-2.548027	0.281983
C	-2.959622	0.410504	-1.913360
C	-3.364641	-3.676310	0.658044
C	-4.179143	0.758710	-2.713487
H	-4.357717	-3.275989	0.891022
H	-4.838795	-0.117761	-2.738640
H	-3.438602	-4.414659	-0.143381
H	-4.732463	1.582724	-2.254610
H	-2.991870	-4.152422	1.572730
H	-3.897936	0.998160	-3.742655
H	2.238929	2.663760	-3.538747
C	-2.421883	1.361919	2.058901
F	-1.550373	1.979937	2.834887
F	-3.254619	2.232630	1.544011
F	-3.073815	0.463259	2.759569

Structure B

(optimized by M06/BS1)

E (BS1) = -2385.25344878 au

H (BS1) = -2384.692743 au

G(BS1) = -2384.809328 au

E(M06/BS2//M06/BS1, Solvent = CH_2Cl_2) = -2388.28981153 au

E(BP86/BS2//M06/BS1, Solvent = CH_2Cl_2) = -2389.87043061 au

E(TPSS/BS2//M06/BS1, Solvent = CH_2Cl_2) = -2389.86983886 au

E(wB97XD/BS2//M06/BS1, Solvent = CH_2Cl_2) = -2388.97595176 au

Pd	-1.740692	0.047163	0.319334
Pd	0.284750	-1.597358	-0.345126
O	-1.998917	-1.388555	1.922974
N	1.315154	-0.098432	-1.309853
C	-0.152007	1.058493	2.715778
C	1.204945	0.266249	-2.575833
H	-0.572486	0.189331	3.218112
H	0.425685	-0.229056	-3.152458
C	0.752782	1.928207	3.336221
C	2.044272	1.245166	-3.124271
H	1.916534	1.527374	-4.166146
C	1.282255	2.987963	2.624460
C	3.004935	1.844273	-2.333399
H	2.005045	3.660695	3.086017
H	3.660298	2.613803	-2.741945
C	0.889326	3.203929	1.293022
C	3.155731	1.441730	-0.995040
C	-0.083129	3.505686	-1.381041

C	3.407725	0.361982	1.643630
C	-0.616618	3.604899	-2.679932
C	3.516613	-0.264679	2.900627
H	-0.303639	4.423970	-3.327072
H	4.277667	0.072727	3.604549
C	-1.540127	2.676440	-3.122490
C	2.685356	-1.323211	3.219940
H	-1.960292	2.773799	-4.122801
H	2.800142	-1.820163	4.183039
C	-1.962176	1.598909	-2.313817
C	1.697663	-1.792657	2.327127
H	-2.700301	0.893841	-2.691461
H	1.083674	-2.654254	2.586515
C	-1.433245	1.471865	-1.050174
C	1.544717	-1.162060	1.112011
C	-0.522136	2.434385	-0.576038
C	2.410501	-0.106503	0.766076
C	-0.038340	2.300471	0.748496
C	2.287625	0.440305	-0.533036
O	-2.881694	-1.097152	-0.929889
O	-0.765819	-2.944545	0.853274
O	-1.105588	-1.969859	-2.016694
N	-0.525267	1.248709	1.456728
C	-2.328057	-1.830522	-1.827769
C	-1.585818	-2.565935	1.738812
C	-3.292734	-2.585084	-2.701039
C	-2.077107	-3.623352	2.691240
H	-3.442294	-3.580629	-2.264945
H	-3.142907	-3.482106	2.895450
H	-4.262233	-2.082152	-2.754601
H	-1.885813	-4.623841	2.295035
H	-2.863581	-2.720224	-3.698200
H	-1.541075	-3.514242	3.643433
H	1.048435	1.734976	4.363800
O	1.543508	-3.339723	-0.904262
C	2.680725	-3.150852	-1.474801
C	3.370512	-4.456891	-1.856487
H	3.580090	-5.041210	-0.952176
H	2.707146	-5.064282	-2.483427
H	4.306167	-4.255678	-2.387682
O	3.225337	-2.071895	-1.718099
C	-3.502626	1.107537	0.823779
F	-4.143914	0.443608	1.781946
F	-4.329789	1.233419	-0.212499
F	-3.242144	2.338918	1.287261
C	1.353202	4.264371	0.447311
H	2.088513	4.961223	0.848628
C	0.885508	4.406940	-0.824556
H	1.243997	5.226350	-1.448016
C	4.245324	1.434899	1.185929
H	5.006666	1.821940	1.864258
C	4.128082	1.948974	-0.071582
H	4.794604	2.743613	-0.407353

Structure C

(optimized by M06/BS1)

E (BS1) = -2385.23561626 au

H (BS1) = -2384.675740 au

G(BS1) = -2384.790038 au

E(M06/BS2//M06/BS1, Solvent = CH_2Cl_2) = -2388.26914466 au

E(BP86/BS2//M06/BS1, Solvent = CH_2Cl_2) = -2389.84081703 au

E(TPSS/BS2//M06/BS1, Solvent = CH_2Cl_2) = -2389.86701062 au

E(wB97XD/BS2//M06/BS1, Solvent = CH_2Cl_2) = -2388.95201030 au

Pd	0.250468	-1.587650	0.407505
Pd	1.464856	0.711819	-0.680206
O	1.555225	-1.343273	2.081858
N	-0.419086	1.175050	-1.455817
C	-0.946711	0.070793	2.662522
C	-0.911226	0.844534	-2.641214
H	0.034386	-0.082235	3.111214
H	-0.352334	0.098566	-3.203433
C	-1.963746	0.833567	3.252029
C	-2.103285	1.404715	-3.122331
H	-2.477514	1.095292	-4.094845
C	-3.173140	0.982475	2.601132
C	-2.799896	2.304916	-2.339534
H	-3.968059	1.585400	3.040209
H	-3.747320	2.722536	-2.681192
C	-3.386782	0.354879	1.361111
C	-2.267661	2.707638	-1.102705
C	-3.625789	-1.006298	-1.141058
C	-0.930594	3.527395	1.291729
C	-3.679782	-1.695394	-2.367698
C	-0.197766	3.906948	2.432386
H	-4.597100	-1.671360	-2.955719
H	-0.615005	4.642533	3.120508
C	-2.579082	-2.401324	-2.815619
C	1.055554	3.363507	2.661996
H	-2.636257	-2.940125	-3.760641
H	1.618673	3.677938	3.540576
C	-1.375474	-2.446827	-2.080031
C	1.642657	2.434518	1.777384
H	-0.531534	-3.023583	-2.454165
H	2.648877	2.051909	1.946095
C	-1.295203	-1.767047	-0.886795
C	0.929870	2.028439	0.668402
C	-2.422062	-1.070417	-0.407946
C	-0.350050	2.568166	0.436065
C	-2.320837	-0.395042	0.835782
C	-1.039097	2.138290	-0.722967
O	1.513080	-2.668034	-0.749041
O	3.189621	-0.779221	0.664022
O	1.984214	-0.912577	-2.101238
N	-1.136451	-0.513987	1.488089
C	2.169602	-2.066923	-1.684606
C	2.785728	-1.082746	1.787127
C	3.268288	-2.900624	-2.278685
C	3.734129	-1.160811	2.961338
H	4.176255	-2.667356	-1.706797
H	3.726002	-2.172727	3.383017
H	3.066019	-3.971333	-2.188048
H	4.747869	-0.892356	2.652855
H	3.438489	-2.615244	-3.320657
H	3.396821	-0.480267	3.753378
H	-1.774093	1.315481	4.207393
O	3.452467	1.621460	-0.584205
C	3.348575	2.602797	-1.406467
C	4.634878	3.375986	-1.625001
H	5.131892	3.572143	-0.668433
H	5.320695	2.768226	-2.228266
H	4.436050	4.315290	-2.149791
O	2.314372	2.918983	-2.012120
C	-0.341399	-3.435264	1.152594

F	0.638932	-3.919442	1.887175
F	-0.603847	-4.300926	0.186895
F	-1.426803	-3.303463	1.911621
C	-4.590180	0.429527	0.586969
H	-5.419143	1.020387	0.975431
C	-4.702644	-0.225262	-0.602513
H	-5.629085	-0.163346	-1.173911
C	-2.220845	4.045095	0.934210
H	-2.681622	4.782342	1.592882
C	-2.855530	3.664715	-0.211572
H	-3.818494	4.098919	-0.480955

Structure D

(optimized by M06/BS1)

E (BS1) = -2385.2597535 au

H (BS1) = -2384.697839 au

G(BS1) = -2384.809347 au

E(M06/BS2//M06/BS1, Solvent = CH_2Cl_2) = -2388.29265303 au

Pd	0.833199	-1.196923	0.465134
Pd	0.839902	1.220944	-1.024269
O	2.104571	-0.097895	1.714110
N	-1.045735	0.758142	-1.795853
C	-0.603956	0.399258	2.630883
C	-1.355990	-0.051441	-2.798115
H	0.416515	0.683579	2.891444
H	-0.522209	-0.568739	-3.270791
C	-1.748914	0.895756	3.269939
C	-2.683361	-0.243136	-3.206811
H	-2.893955	-0.921440	-4.029428
C	-2.998874	0.492030	2.845106
C	-3.700348	0.409098	-2.537697
H	-3.898714	0.882269	3.321477
H	-4.741629	0.254654	-2.822323
C	-3.121466	-0.423079	1.784004
C	-3.393710	1.283783	-1.480963
C	-3.158077	-2.311037	-0.362528
C	-2.569414	3.082867	0.581679
C	-3.105780	-3.236711	-1.422653
C	-2.097650	3.956603	1.580036
H	-4.033336	-3.656953	-1.811765
H	-2.808508	4.555213	2.150256
C	-1.887377	-3.606885	-1.961523
C	-0.739718	4.051508	1.827657
H	-1.860256	-4.331459	-2.774790
H	-0.385471	4.734452	2.599840
C	-0.671849	-3.069923	-1.487515
C	0.205227	3.291436	1.107717
H	0.276040	-3.383701	-1.922848
H	1.268871	3.372437	1.328504
C	-0.698197	-2.158833	-0.456137
C	-0.227325	2.432851	0.115750
C	-1.932783	-1.803432	0.120160
C	-1.612266	2.336857	-0.138392
C	-1.929469	-0.882120	1.200080
C	-2.034018	1.441137	-1.156685
O	2.143285	-2.032113	-0.825159
O	4.044126	-0.477755	0.617919
O	2.012015	-0.234086	-2.185371

N	-0.712089	-0.461961	1.630769
C	2.542095	-1.291906	-1.798358
C	3.384814	0.056916	1.495284
C	3.765265	-1.810312	-2.491547
C	4.008771	1.016975	2.488873
H	4.617545	-1.496913	-1.874906
H	3.734132	0.754661	3.517572
H	3.766631	-2.903590	-2.534953
H	5.097839	1.017893	2.382207
H	3.857800	-1.373557	-3.489478
H	3.621980	2.023191	2.282700
H	-1.632788	1.614613	4.076442
O	2.552856	1.945399	-0.206348
C	3.133334	2.648519	-1.136299
C	4.537689	3.057792	-0.768018
H	4.518855	3.712980	0.112215
H	5.108258	2.162079	-0.491658
H	5.019344	3.577937	-1.600512
O	2.599509	2.942357	-2.202841
C	-4.355640	-0.926921	1.257795
H	-5.287802	-0.568073	1.693811
C	-4.369650	-1.835000	0.241882
H	-5.318926	-2.215649	-0.136486
C	1.158838	-2.900344	1.573020
F	2.389388	-2.866954	2.028830
F	0.999856	-4.001419	0.859624
F	0.308394	-2.925054	2.594125
C	-3.955107	2.887061	0.263289
H	-4.699189	3.453383	0.824878
C	-4.351651	2.029638	-0.719312
H	-5.409197	1.902080	-0.950894

Structure E

(optimized by M06/BS1)

E (BS1) = -2385.25240435 au

H (BS1) = -2384.692273 au

G(BS1) = -2384.806315 au

E(M06/BS2//M06/BS1, Solvent = CH_2Cl_2) = -2388.28617677 au

Pd	0.83319900	-1.19692300	0.46513400
Pd	0.77919900	1.64531800	-1.08890400
O	2.07016100	0.01422400	1.63541800
N	-1.08348000	1.03145900	-1.80217000
C	-0.63602000	0.52193600	2.52869700
C	-1.36370100	0.13056800	-2.73408500
H	0.37573700	0.86613100	2.74721600
H	-0.51032300	-0.37282000	-3.18597200
C	-1.78876100	1.02584100	3.14848300
C	-2.68351700	-0.15737500	-3.11032100
H	-2.86548800	-0.91114900	-3.87201100
C	-3.02651900	0.52401400	2.80037100
C	-3.72536200	0.50643700	-2.49300100
H	-3.93182400	0.90679500	3.27183500
H	-4.75998900	0.28840700	-2.75980800
C	-3.13116900	-0.47471200	1.81426700
C	-3.45273900	1.46928300	-1.50577900
C	-3.14739300	-2.36773100	-0.32630400
C	-2.70320500	3.34361400	0.51976800
C	-3.08974400	-3.26647100	-1.40965900

C	-2.26840300	4.24412100	1.51135900
H	-4.01352500	-3.69956900	-1.79353100
H	-3.00409300	4.80859000	2.08485700
C	-1.87285600	-3.60028600	-1.97433400
C	-0.91404700	4.41672300	1.73978900
H	-1.84387100	-4.30281300	-2.80648500
H	-0.58911600	5.12153200	2.50524900
C	-0.66006600	-3.05890500	-1.49661500
C	0.06339400	3.71556800	1.00386900
H	0.28930800	-3.34710800	-1.94624500
H	1.12431600	3.86972300	1.19652800
C	-0.69272700	-2.17264200	-0.44491600
C	-0.33253500	2.82769500	0.02188700
C	-1.92756400	-1.83728000	0.14516900
C	-1.71516600	2.64301100	-0.20423400
C	-1.93482300	-0.90430500	1.21598600
C	-2.10063600	1.69832100	-1.19135000
O	2.17399600	-1.96395100	-0.82282100
O	4.00067300	-0.19106200	0.48359400
O	1.92210600	-0.07911100	-2.03252000
N	-0.72541500	-0.42530100	1.60627600
C	2.53940200	-1.10936600	-1.72766000
C	3.32702600	0.27660100	1.39002100
C	3.81260700	-1.47502200	-2.42510100
C	3.89757900	1.26371900	2.38667200
H	4.61863500	-1.08994300	-1.78681400
H	3.67872400	0.95248700	3.41502600
H	3.93128700	-2.55968600	-2.50753200
H	4.97849400	1.36225300	2.24779700
H	3.86337100	-0.99302700	-3.40504400
H	3.41859100	2.23579400	2.21513000
H	-1.68660900	1.81670500	3.88640000
O	2.47327700	2.40374300	-0.26274700
C	3.24126300	2.78912500	-1.24592500
C	4.66938100	3.03355500	-0.82520700
H	4.71092500	3.66039800	0.07349800
H	5.12226500	2.06533100	-0.57143300
H	5.23112400	3.50377000	-1.63731600
O	2.86053000	2.91139500	-2.40552600
C	-4.35626100	-1.04558800	1.33678600
H	-5.29007600	-0.72670200	1.79896900
C	-4.36045100	-1.94923400	0.31698100
H	-5.30296800	-2.36610900	-0.03872600
C	1.17718300	-2.87184100	1.56764600
F	2.37999300	-2.75858100	2.07790000
F	1.11441500	-3.96905000	0.84316300
F	0.28070800	-2.93793700	2.54148400
C	-4.07939900	3.09590100	0.19461200
H	-4.84637500	3.64669600	0.74058300
C	-4.44018500	2.20953700	-0.77619800
H	-5.49130300	2.04111600	-1.01076400

Structure F

(optimized by M06/BS1)

E (BS1) = -2385.25358776 au

H (BS1) = -2384.691364 au

G(BS1) = -2384.807530 au

E(M06/BS2//M06/BS1, Solvent = CH_2Cl_2) = -2388.28754324 au

Pd	-2.007806	-1.066554	0.393992
Pd	2.275160	-0.607999	-0.522208
O	-1.095000	-1.941829	2.209655
N	1.817876	1.365232	-0.994524
C	-2.951552	0.542605	2.811510
C	0.756918	1.833167	-1.635235
H	-2.648703	-0.343144	3.368631
H	0.057212	1.085212	-2.007704
C	-3.429035	1.707106	3.425920
C	0.551646	3.208285	-1.818148
H	-0.335373	3.544437	-2.351641
C	-3.763457	2.800810	2.649874
C	1.478024	4.105018	-1.321465
H	-4.129594	3.716191	3.114190
H	1.342879	5.178679	-1.456624
C	-3.629946	2.740314	1.251621
C	2.604665	3.631321	-0.626892
C	-3.298722	2.407105	-1.569146
C	4.783792	2.476674	0.820571
C	-3.121742	2.175077	-2.946443
C	5.812919	1.852847	1.550128
H	-3.350032	2.968740	-3.657403
H	6.594799	2.460506	2.005928
C	-2.673265	0.945777	-3.392952
C	5.817744	0.476973	1.689342
H	-2.545343	0.777481	-4.461084
H	6.616303	0.002663	2.259960
C	-2.369822	-0.106454	-2.501814
C	4.818450	-0.335094	1.116044
H	-2.004567	-1.057550	-2.880952
H	4.839712	-1.414771	1.259583
C	-2.520946	0.112825	-1.154701
C	3.803324	0.241562	0.376389
C	-2.990418	1.351598	-0.685002
C	3.797583	1.650244	0.241133
C	-3.157126	1.532179	0.711851
C	2.725699	2.236310	-0.480611
O	-1.227730	-2.606747	-0.650208
O	-0.085350	-0.301624	1.158286
O	0.370697	-1.307441	-1.517677
N	-2.832040	0.474414	1.493525
C	-0.117273	-2.421760	-1.293931
C	-0.070202	-1.200440	2.055825
C	0.490087	-3.697889	-1.804305
C	1.159748	-1.410773	2.873105
H	0.595996	-4.413356	-0.981122
H	0.931774	-1.950111	3.797236
H	-0.188655	-4.148566	-2.538937
H	1.859522	-2.005320	2.263798
H	1.464737	-3.494373	-2.258475
H	1.648262	-0.452803	3.080703
H	-3.523863	1.734800	4.507799
O	2.772650	-2.453920	0.242820
C	3.458727	-3.206944	-0.566479
C	3.929348	-4.493672	0.084163
H	3.101661	-4.989750	0.605710
H	4.358004	-5.165542	-0.664815
H	4.691853	-4.266532	0.840935
O	3.718560	-2.947831	-1.735989
C	-3.785549	-1.995087	0.088215
F	-3.798474	-2.992263	0.964793
F	-3.944703	-2.491341	-1.126768
F	-4.823941	-1.196317	0.346875
C	-3.930073	3.803095	0.337545
H	-4.292180	4.747721	0.741440
C	-3.768803	3.640675	-1.005348
H	-4.004011	4.460122	-1.684406
C	4.664553	3.895799	0.641209

H	5.430180	4.536562	1.080250
C	3.626570	4.451139	-0.044984
H	3.552562	5.532654	-0.159180

Structure G

(optimized by M06/BS1)

E (BS1) = -2385.25143095 au

H (BS1) = -2384.689759 au

G(BS1) = -2384.804474 au

E(M06/BS2//M06/BS1, Solvent = CH_2Cl_2) = -2388.28138147 au

Pd	1.233962	-1.498816	-0.714669
Pd	-3.037614	0.284205	0.621650
O	0.037466	-1.766852	-2.571473
N	-1.480211	1.115903	1.707482
C	1.920621	0.707911	-2.731905
C	-0.911187	0.625937	2.798118
H	1.384094	0.067264	-3.430142
H	-1.338836	-0.292145	3.193881
C	2.420746	1.967406	-3.082925
C	0.204770	1.244738	3.382454
H	0.643394	0.811803	4.278078
C	3.082686	2.725318	-2.136111
C	0.742087	2.375336	2.801632
H	3.476501	3.708975	-2.391447
H	1.613589	2.863802	3.240108
C	3.253719	2.229569	-0.833106
C	0.163495	2.901193	1.632054
C	3.517394	1.041069	1.751078
C	-1.181216	3.818525	-0.722237
C	3.634366	0.398848	2.996307
C	-1.898072	4.212593	-1.869277
H	4.184154	0.886172	3.801722
H	-1.583884	5.096368	-2.425147
C	3.056669	-0.841605	3.190617
C	-2.998951	3.480674	-2.276379
H	3.157020	-1.334641	4.156801
H	-3.552049	3.798890	-3.160282
C	2.332527	-1.495522	2.172796
C	-3.429849	2.327716	-1.583497
H	1.880361	-2.463583	2.364391
H	-4.294541	1.767701	-1.941901
C	2.210805	-0.883229	0.948284
C	-2.746115	1.911961	-0.457943
C	2.809715	0.370364	0.729415
C	-1.635132	2.673527	-0.037116
C	2.713014	0.961142	-0.557469
C	-0.962298	2.229859	1.126112
O	0.317451	-3.133322	-0.013148
O	-0.713475	-0.495138	-0.950485
O	-0.575821	-2.012471	1.730698
N	2.071535	0.232839	-1.502829
C	-0.535451	-2.968190	0.977306
C	-0.884711	-1.043507	-2.081976
C	-1.488998	-4.136791	1.071885
C	-2.156225	-0.816642	-2.835373
H	-2.168604	-4.107094	0.210806
H	-2.181601	-1.424828	-3.743917
H	-0.948069	-5.088341	1.026806

H	-3.017952	-1.041169	-2.192003
H	-2.075864	-4.061238	1.990665
H	-2.237064	0.247081	-3.094981
H	2.278380	2.331494	-4.096581
O	-4.563394	-0.733713	-0.406599
C	-4.531060	-1.715542	0.419025
C	-5.428033	-2.888557	0.161157
H	-6.474298	-2.561613	0.148165
H	-5.210606	-3.311742	-0.827009
H	-5.289229	-3.653641	0.930527
O	-3.755348	-1.691258	1.406444
C	2.869800	-2.655164	-0.989902
F	2.606417	-3.357059	-2.085848
F	3.120130	-3.497647	-0.000427
F	3.970927	-1.933774	-1.212223
C	3.932667	2.910239	0.229511
H	4.352959	3.895533	0.029831
C	4.068553	2.333126	1.455592
H	4.604543	2.855857	2.248653
C	-0.019236	4.488187	-0.208347
H	0.344875	5.369850	-0.738102
C	0.625766	4.052471	0.911769
H	1.511954	4.570768	1.281044

Pd(IV) fragment of Structure G

(optimized by M06/BS1)

E (BS1) = -1475.53269682 au

H (BS1) = -1475.214821 au

G(BS1) = -1475.297780 au

E(M06/BS2//M06/BS1, Solvent = CH_2Cl_2) = -1477.14829983 au

Pd	0.761049	0.221420	0.151391
O	1.874776	2.152072	0.164083
C	-1.190190	2.578521	0.333753
H	-0.290324	3.142323	0.576001
C	-2.456608	3.166681	0.232661
C	-3.548672	2.382543	-0.087304
H	-4.540981	2.825072	-0.173453
C	-3.386616	1.003739	-0.303706
C	-2.851915	-1.776684	-0.678125
C	-2.533644	-3.137654	-0.830063
H	-3.322197	-3.848312	-1.075541
C	-1.231862	-3.566327	-0.660511
H	-0.995157	-4.622691	-0.777753
C	-0.186423	-2.674977	-0.340847
H	0.826260	-3.048277	-0.228995
C	-0.477924	-1.340210	-0.205002
C	-1.800678	-0.888082	-0.361929
C	-2.083437	0.489375	-0.178912
O	2.533080	-0.704650	0.236621
O	1.280029	1.251547	-1.754474
O	2.262386	-1.756080	-1.746120
N	-1.026699	1.278702	0.129157
C	2.937201	-1.415669	-0.794419
C	1.877931	2.156793	-1.106965
C	4.398858	-1.784016	-0.641966
C	2.589821	3.246511	-1.852604
H	5.010805	-0.874654	-0.641518
H	3.054941	3.955851	-1.162992

H	4.569594	-2.287437	0.316151
H	3.354155	2.801132	-2.499371
H	4.700789	-2.432475	-1.468849
H	1.882922	3.769108	-2.507366
H	-2.562016	4.233807	0.408065
C	0.581150	-0.316374	2.093956
F	1.413566	0.493261	2.738211
F	0.919425	-1.568279	2.353820
F	-0.648344	-0.111779	2.571542
C	-4.436039	0.086752	-0.636781
H	-5.448779	0.473385	-0.743582
C	-4.174589	-1.237777	-0.814072
H	-4.983547	-1.923872	-1.064905

Pd(II) fragment of Structure G

(optimized by M06/BS1)

E (BS1) = -909.693380229 au

H (BS1) = -909.452238 au

G(BS1) = -909.514575 au

E(M06/BS2//M06/BS1, Solvent = CH_2Cl_2) = -911.120338273 au

Pd	-1.211169	-0.108619	0.000375
N	0.451330	-1.341284	0.000914
C	0.475522	-2.667691	0.000703
H	-0.493031	-3.166326	0.001250
C	1.680931	-3.382548	-0.000023
H	1.655264	-4.468881	-0.000341
C	2.879999	-2.695066	-0.000495
H	3.827645	-3.233882	-0.001037
C	2.879525	-1.289788	-0.000330
C	2.654946	1.565090	-0.000169
C	2.462730	2.960123	-0.000085
H	3.327850	3.622990	-0.000302
C	1.180248	3.478270	0.000279
H	1.044799	4.559549	0.000380
C	0.036846	2.650471	0.000493
H	-0.958117	3.095059	0.000656
C	0.192896	1.279931	0.000466
C	1.501962	0.755485	0.000205
C	1.624987	-0.654794	0.000291
O	-2.975579	0.984336	-0.000751
C	-3.696886	-0.074758	-0.000737
C	-5.185352	0.080501	-0.001044
H	-5.496472	0.646887	0.884438
H	-5.495231	0.658856	-0.879138
H	-5.675042	-0.896901	-0.007661
O	-3.151416	-1.209840	-0.000150
C	3.931764	0.907804	-0.000728
H	4.830472	1.525355	-0.001067
C	4.042926	-0.451019	-0.000861
H	5.024013	-0.925297	-0.001405

Structure H

(optimized by M06/BS1)

E (BS1) = -1551.95345847 au

H (BS1) = -1551.606365 au

G(BS1) = -1551.689713 au

E(M06/BS2//M06/BS1, Solvent = CH_2Cl_2) = -1553.60037652 au

Pd	-0.736070	0.110834	-0.134297	H	3.282980	-3.688457	1.816304
N	1.062350	0.995486	-0.666539	C	1.170640	-3.349465	1.616679
O	-1.782533	1.860061	-0.982460	H	0.907689	-4.285851	2.106737
H	-2.711532	1.543715	-0.833462	C	0.131045	-2.507969	1.163658
H	-1.567401	2.496115	-0.237942	H	-0.913922	-2.779719	1.295485
O	-2.325095	-0.951391	0.533164	C	0.476000	-1.334173	0.549350
O	-3.908973	0.482365	-0.219034	C	1.821140	-0.975493	0.375261
O	-0.537899	1.050519	1.782885	C	2.123375	0.252785	-0.263186
O	-0.805618	3.171116	1.068269	C	-0.911799	-0.936935	-1.871489
C	1.243908	2.158337	-1.273959	C	-3.547443	-0.535206	0.364178
H	0.346653	2.699737	-1.567261	C	-4.547708	-1.480303	0.986705
C	2.536156	2.644645	-1.514712	H	-5.561009	-1.101807	0.830647
H	2.655264	3.602287	-2.013742	H	-4.347248	-1.581642	2.059153
C	3.631801	1.905585	-1.113156	H	-4.447322	-2.475702	0.539345
H	4.642003	2.273012	-1.292905	C	-0.557873	2.322404	1.942448
C	3.449176	0.670501	-0.466879	C	-0.253894	2.769464	3.355073
C	4.496333	-0.191668	-0.002313	H	0.693087	2.333965	3.693657
H	5.529070	0.120598	-0.152811	H	-1.034953	2.397795	4.029043
C	4.213211	-1.373957	0.612463	H	-0.210680	3.860424	3.413662
H	5.023701	-2.015233	0.958576	F	-1.160341	-2.227647	-1.667290
C	2.863635	-1.812383	0.826123	F	-1.923600	-0.433617	-2.570489
C	2.502712	-3.018676	1.456015	F	0.192257	-0.851218	-2.619688

Structure I

(optimized by M06/BS1)

E (BS1) = -1819.451697 au

H (BS1) = -1818.967087 au

G(BS1) = -1819.063262 au

E(M06/BS2//M06/BS1, Solvent = CH_2Cl_2) = -1822.29296708 au

Pd	1.297863	-0.746809	-1.240464
Pd	1.297903	0.746788	1.240455
O	2.532664	0.995739	-1.679230
N	-0.457948	0.133923	-1.906151
N	-0.457916	-0.133906	1.906174
C	0.079489	-2.264360	-0.883283
C	0.079553	2.264366	0.883301
O	2.909124	-1.753903	-0.420267
O	2.532664	-0.995793	1.679207
O	2.909177	1.753843	0.420235
C	3.136437	-1.694306	0.827742
C	3.136481	1.694224	-0.827775
C	-0.625857	1.361113	-2.379801
H	0.284273	1.927592	-2.571698
C	-1.902710	1.895045	-2.604386
H	-1.994976	2.908288	-2.986760
C	-3.018318	1.134467	-2.314031
H	-4.020503	1.537035	-2.465261
C	-2.863840	-0.168784	-1.809973
C	-1.548061	-0.628273	-1.619652
C	-1.276052	-1.921002	-1.099107
C	-2.344829	-2.790658	-0.795832
C	-2.024898	-4.065244	-0.289905
H	-2.825312	-4.767128	-0.054259
C	-0.700593	-4.416742	-0.100632
H	-0.462570	-5.409108	0.282668
C	0.354780	-3.524466	-0.383133
H	1.386230	-3.830123	-0.208793
C	-0.625842	-1.361091	2.379832
H	0.284281	-1.927581	2.571731
C	-1.902702	-1.895012	2.604401
H	-1.994980	-2.908256	2.986769
C	-3.018300	-1.134424	2.314035
H	-4.020490	-1.536980	2.465258
C	-2.863804	0.168827	1.809981
C	-1.548019	0.628301	1.619667
C	-1.275992	1.921026	1.099123
C	-2.344757	2.790697	0.795849
C	-2.024808	4.065281	0.289928
H	-2.825214	4.767176	0.054283
C	-0.700499	4.416766	0.100667
H	-0.462462	5.409131	-0.282625
C	0.354862	3.524474	0.383164
H	1.386316	3.830121	0.208832
C	4.259585	-2.566045	1.333742
H	5.086876	-1.926404	1.663814
H	4.617733	-3.248797	0.558794
H	3.921886	-3.130107	2.210423
C	4.259600	2.565984	-1.333803
H	5.086896	1.926353	-1.663880
H	4.617748	3.248751	-0.558868
H	3.921878	3.130032	-2.210486
C	-3.683343	-2.311432	-0.995334
C	-3.934647	-1.057111	-1.465778
H	-4.958824	-0.707913	-1.599325
H	-4.511779	-2.977800	-0.750973
C	-3.934600	1.057165	1.465776
H	-4.958781	0.707981	1.599322
C	-3.683278	2.311486	0.995338
H	-4.511704	2.977866	0.750981

Structure J

(optimized by M06/BS1)

E (BS1) = -2156.69480347 au

H (BS1) = -2156.191520 au

G(BS1) = -2156.293604 au

E(M06/BS2//M06/BS1, Solvent = CH_2Cl_2) = -2159.67392680 au

E(BP86/BS2//M06/BS1, Solvent = CH_2Cl_2) = -2161.10808469 au

E(TPSS/BS2//M06/BS1, Solvent = CH_2Cl_2) = -2161.11094573 au

E(wB97XD/BS2//M06/BS1, Solvent = CH_2Cl_2) = -2160.30261025 au

Pd	1.593873	-0.014880	-0.594884	H	1.424065	4.490827	2.040042
Pd	0.170760	-1.486127	1.319698	H	-2.860313	-4.418576	-1.736260
O	1.987321	-2.001812	-1.246329	C	1.714210	2.751949	0.800595
N	-1.166546	-0.015125	1.906429	C	-1.540721	-3.267428	-0.473516
C	-0.566535	-0.781204	-2.604422	H	2.736427	2.589830	1.135696
C	-0.960748	0.993679	2.743394	H	-0.721567	-3.979046	-0.571914
H	0.061687	-1.649310	-2.796222	C	1.144555	1.926820	-0.155770
H	0.031614	1.056892	3.187817	C	-1.408806	-2.139522	0.311155
C	-1.842345	-0.632535	-3.165814	C	-0.180912	2.172685	-0.599105
C	-1.969576	1.924611	3.029382	C	-2.519053	-1.276480	0.449563
H	-1.763772	2.731994	3.727389	C	-0.785160	1.258036	-1.497039
C	-2.605992	0.470636	-2.842867	C	-2.382253	-0.156891	1.308731
C	-3.205593	1.798774	2.425296	O	3.165567	-0.091252	0.676817
H	-3.611693	0.584379	-3.246985	O	1.351782	-3.038927	0.650693
H	-4.001742	2.512093	2.638707	O	1.867704	-0.664366	2.432820
C	-2.091736	1.453369	-1.975260	N	-0.062520	0.147187	-1.803257
C	-3.445077	0.735504	1.535580	C	2.964354	-0.368363	1.917118
C	-0.919934	3.269543	-0.120568	C	1.925696	-3.002844	-0.474281
C	-3.750445	-1.519492	-0.194375	C	4.195321	-0.332896	2.774843
C	-0.305619	4.104932	0.837831	C	2.553966	-4.276897	-0.962843
C	-3.847292	-2.667235	-1.005495	H	4.634021	-1.338452	2.790969
H	-0.850962	4.970289	1.213479	H	1.913990	-4.707110	-1.744231
H	-4.786021	-2.889055	-1.512505	H	4.943741	0.356397	2.374724
C	0.970722	3.836823	1.297959	H	3.527713	-4.070164	-1.416806
C	-2.765995	-3.519315	-1.128937	H	3.927905	-0.069694	3.802183

H	2.651920	-5.000100	-0.149981
H	-2.218232	-1.401575	-3.834703
C	2.509956	1.826821	-1.698851
F	2.697719	1.018041	-2.740431
F	3.656657	2.039795	-1.103940
F	2.034183	2.953296	-2.196797
C	-2.255479	3.457759	-0.607570
H	-2.824544	4.311718	-0.241482
C	-2.813635	2.595948	-1.504025
H	-3.830962	2.749034	-1.861574
C	-4.681446	0.484698	0.854307
H	-5.514583	1.165948	1.023666
C	-4.823737	-0.592561	0.030794
H	-5.778470	-0.777265	-0.461976

Structure K

(optimized by M06/BS1)

E (BS1) = -2156.74358267 au

H (BS1) = -2156.237966 au

G(BS1) = -2156.342807 au

E(M06/BS2//M06/BS1, Solvent = CH_2Cl_2) = -2159.72568040 au

Pd	1.892742	0.348927	0.366758
Pd	-0.289122	1.147102	-1.396453
O	2.210335	2.377514	0.564458
N	-1.574426	-0.407185	-1.849626
C	0.408364	1.329281	2.853496
C	-1.412823	-1.353341	-2.765423
H	1.068345	2.194529	2.821544
H	-0.468071	-1.337519	-3.307868
C	-0.741923	1.284252	3.657509
C	-2.408770	-2.309870	-3.014110
H	-2.246965	-3.059099	-3.785196
C	-1.622128	0.231851	3.524956
C	-3.583827	-2.276814	-2.286654
H	-2.568311	0.227689	4.064586
H	-4.369867	-3.009074	-2.471245
C	-1.320643	-0.824797	2.641916
C	-3.776726	-1.278677	-1.314207
C	-0.653111	-2.661987	0.595398
C	-4.010865	0.879070	0.545266
C	-0.347553	-3.424962	-0.550232
C	-4.090734	1.998620	1.396583
H	-1.102679	-4.106324	-0.942716
H	-4.981078	2.149032	2.006407
C	0.874543	-3.301995	-1.199492
C	-3.061620	2.921400	1.418323
H	1.061995	-3.858000	-2.115269
H	-3.147016	3.800429	2.056500
C	1.902453	-2.582479	-0.603764
C	-1.905990	2.770255	0.620777
H	2.915615	-2.647205	-0.999062
H	-1.130944	3.536641	0.644683
C	1.702304	-1.856871	0.596302
C	-1.781472	1.667503	-0.200801
C	0.340751	-1.801601	1.099145
C	-2.842322	0.732436	-0.232048
C	-0.066321	-0.783678	2.008064
C	-2.733720	-0.350259	-1.138483
O	3.014631	0.306476	-1.312492

O	0.727161	2.929684	-1.049539
O	1.268120	0.407904	-2.742373
N	0.729933	0.319215	2.062231
C	2.486967	0.319116	-2.480649
C	1.627010	3.196145	-0.216286
C	3.471098	0.232033	-3.613094
C	2.042678	4.634501	-0.077957
H	3.763721	1.250882	-3.896058
H	1.490361	5.083276	0.758197
H	4.374931	-0.307033	-3.316571
H	3.109744	4.707904	0.148761
H	3.003360	-0.235525	-4.484086
H	1.799104	5.189550	-0.987296
H	-0.954741	2.113145	4.327119
C	2.867967	-2.061110	1.573764
F	2.758031	-1.384268	2.711669
F	4.027044	-1.744386	1.000732
F	2.916564	-3.358219	1.896357
C	-1.940979	-2.689903	1.228750
H	-2.680334	-3.400084	0.859980
C	-2.243119	-1.847825	2.253748
H	-3.223827	-1.875598	2.726350
C	-4.948166	-1.123607	-0.502423
H	-5.763740	-1.835202	-0.625653
C	-5.051889	-0.097939	0.389911
H	-5.957961	0.012786	0.985662

Structure K´

(optimized by M06/BS1)

E (BS1) = -2156.73939732 au

H (BS1) = -2156.233487 au

G(BS1) = -2156.338741 au

E(M06/BS2//M06/BS1, Solvent = CH_2Cl_2) = -2159.71733633 au

Pd	2.286945	0.084418	0.298244
Pd	0.097119	-1.028780	-1.379154
O	2.936022	0.900077	-1.435785
N	-1.526846	-1.916271	-0.471414
C	2.133306	2.948790	0.326188
C	-1.568696	-3.090993	0.145327
H	3.169306	2.749553	0.064247
H	-0.615639	-3.604481	0.262561
C	1.578362	4.212311	0.126135
C	-2.778581	-3.637354	0.596114
H	-2.772519	-4.606982	1.086881
C	0.221117	4.347093	0.291267
C	-3.957493	-2.944313	0.397305
H	-0.284800	5.281181	0.049382
H	-4.907319	-3.358711	0.735114
C	-0.541887	3.271264	0.778099
C	-3.933017	-1.696094	-0.250314
C	-2.053502	1.132862	1.775871
C	-3.668538	0.823406	-1.578614
C	-2.860345	0.099308	2.292782
C	-3.466978	2.061644	-2.218521
H	-3.941685	0.192829	2.194706
H	-4.319194	2.710943	-2.416908
C	-2.306942	-0.979515	2.937311
C	-2.192729	2.441982	-2.593210
H	-2.932828	-1.776701	3.331772

H	-2.045232	3.403601	-3.084186
C	-0.928507	-0.991072	3.168827
C	-1.070564	1.611063	-2.377151
H	-0.504094	-1.760873	3.807529
H	-0.089347	1.944778	-2.714477
C	-0.103205	-0.001257	2.661388
C	-1.237157	0.384114	-1.767762
C	-0.632306	1.041310	1.841358
C	-2.536783	0.012708	-1.353825
C	0.116892	2.067130	1.138900
C	-2.679586	-1.223350	-0.676888
O	3.242448	-1.606567	-0.181950
O	1.485552	-0.243454	-2.732609
O	1.407641	-2.714635	-0.887538
N	1.428088	1.910674	0.775892
C	2.616266	-2.653234	-0.590926
C	2.473483	0.497074	-2.559012
C	3.480423	-3.876718	-0.696239
C	3.228074	0.972485	-3.767935
H	4.238967	-3.717283	-1.471421
H	2.529835	1.173963	-4.585499
H	4.013629	-4.045698	0.245113
H	3.830572	1.855202	-3.541145
H	2.875528	-4.748993	-0.954968
H	3.900255	0.168693	-4.092389
H	2.204707	5.029955	-0.218025
C	1.298138	-0.026500	3.193588
F	1.846156	1.168150	3.336650
F	2.140530	-0.739386	2.337896
F	1.398627	-0.666380	4.344395
C	-2.691507	2.303889	1.260975
H	-3.779920	2.336669	1.261732
C	-1.962579	3.369950	0.859645
H	-2.436632	4.296935	0.541159
C	-5.075597	-0.867049	-0.505411
H	-6.055878	-1.222661	-0.190003
C	-4.944370	0.336284	-1.133170
H	-5.825634	0.949779	-1.320700

Structure L

(optimized by M06/BS1)

E (BS1) = -2385.22469071 au

H (BS1) = -2384.665171 au

G(BS1) = -2384.781316 au

E(M06/BS2//M06/BS1, Solvent = CH_2Cl_2) = -2388.25884391 au

E(BP86/BS2//M06/BS1, Solvent = CH_2Cl_2) = -2389.83490402 au

E(TPSS/BS2//M06/BS1, Solvent = CH_2Cl_2) = -2389.86075687 au

E(wB97XD/BS2//M06/BS1, Solvent = CH_2Cl_2) = -2388.93275954 au

Pd	-1.016011	-1.239614	0.467490
Pd	1.522197	-0.892718	-0.274551
O	0.051440	-2.270567	2.197588
N	0.854936	0.703412	-1.407949
C	-0.629834	0.787928	2.727989
C	0.339603	0.674335	-2.625251
H	-0.088068	-0.026390	3.205668
H	0.189086	-0.312423	-3.060413

C	-0.734559	2.065598	3.288277
C	0.007785	1.855747	-3.302089
H	-0.429746	1.791104	-4.294936
C	-1.390354	3.065233	2.593278
C	0.232359	3.075648	-2.696341
H	-1.445806	4.076120	2.997183
H	-0.021264	4.004791	-3.206970
C	-1.982135	2.783521	1.351723
C	0.805341	3.122093	-1.413215
C	-3.038239	2.024816	-1.192719
C	2.031031	3.005096	1.168146
C	-3.506778	1.604236	-2.451073
C	2.678470	2.874312	2.412517
H	-3.964217	2.328583	-3.124216
H	2.933130	3.768635	2.981535
C	-3.382783	0.275995	-2.824953
C	3.020001	1.621280	2.887484
H	-3.737867	-0.038526	-3.805610
H	3.547359	1.534629	3.837209
C	-2.842155	-0.692655	-1.965453
C	2.719526	0.443136	2.169208
H	-2.812432	-1.737143	-2.267557
H	3.035031	-0.529075	2.545095
C	-2.394803	-0.318992	-0.701699
C	2.045662	0.549705	0.973868
C	-2.449421	1.060275	-0.351165
C	1.725483	1.822955	0.464837
C	-1.874777	1.461111	0.877441
C	1.108806	1.892321	-0.808445
O	-0.947328	-2.944024	-0.668416
O	2.004337	-2.393054	1.071057
O	0.918940	-2.369357	-1.792320
N	-1.173405	0.509627	1.548961
C	-0.042298	-3.129204	-1.551542
C	1.208971	-2.707534	2.015825
C	-0.165422	-4.398963	-2.350301
C	1.775916	-3.673429	3.027164
H	-1.165541	-4.832372	-2.266267
H	0.993699	-4.352771	3.378836
H	0.086647	-4.202432	-3.397351
H	2.617855	-4.231682	2.609875
H	0.567292	-5.120281	-1.968479
H	2.134756	-3.101073	3.892926
H	-0.267952	2.260724	4.250134
C	-3.375970	-1.481903	0.645062
O	3.611000	-1.033316	-0.863984
C	4.089729	-0.175150	-1.701468
C	5.531885	-0.493884	-2.078585
H	5.908232	0.244693	-2.792931
H	6.159523	-0.495906	-1.179689
H	5.590311	-1.498019	-2.514316
O	3.517118	0.801820	-2.178293
F	-3.739103	-2.547281	-0.054152
F	-3.165958	-1.883503	1.913698
F	-4.415485	-0.645993	0.716017
C	-2.634149	3.738036	0.505484
H	-2.710640	4.768830	0.850046
C	-3.114865	3.377244	-0.716694
H	-3.581154	4.122210	-1.361689
C	1.101641	4.314733	-0.674872
H	0.862218	5.276624	-1.128004
C	1.681913	4.256385	0.556949
H	1.911688	5.175954	1.096182

Structure M

(optimized by M06/BS1)

E (BS1) = -2386.96571235 au

H (BS1) = -2386.403593 au

G(BS1) = -2386.520684 au

E(M06/BS2//M06/BS1, Solvent = CH_2Cl_2) = -2388.30453837 au

Pd	-0.642533	-1.637098	0.358563	C	2.615819	0.832551	2.168258
Pd	1.651576	-0.614419	-0.323925	H	-4.471044	-1.676367	-2.018295
O	0.925995	-2.464037	2.290217	H	3.086698	-0.081677	2.524443
N	0.597427	0.841810	-1.341283	C	-3.484062	-0.582028	-0.471311
C	-0.650732	0.113340	2.714949	C	1.892651	0.843643	0.995294
C	0.033658	0.745552	-2.534519	C	-2.960015	0.679171	-0.063327
H	-0.016695	-0.716826	3.027561	C	1.365216	2.058805	0.518631
H	0.016124	-0.248104	-2.977747	C	-2.114977	0.912680	1.087443
C	-0.704246	1.318444	3.425688	C	0.699518	2.048525	-0.733779
C	-0.492272	1.870853	-3.181051	O	-0.098755	-3.181640	-0.845077
H	-0.958627	1.752304	-4.155808	O	2.587974	-2.032001	0.813138
C	-1.355561	2.384488	2.854975	O	1.488386	-2.047510	-1.954683
C	-0.398851	3.109798	-2.577607	N	-1.310577	-0.075251	1.574218
H	-1.314504	3.377380	3.303647	C	0.797549	-3.071591	-1.740746
H	-0.791252	4.000302	-3.070366	C	2.069033	-2.605181	1.844964
C	-2.055894	2.210318	1.646898	C	1.049305	-4.289404	-2.585972
C	0.215848	3.229333	-1.320441	C	3.054698	-3.524679	2.537613
C	-3.310576	1.815066	-0.841275	H	0.183237	-4.957019	-2.589745
C	1.538131	3.273837	1.215450	H	2.569133	-4.054071	3.361714
C	-3.893337	1.641320	-2.112273	H	1.317462	-3.992848	-3.604607
C	2.236949	3.230894	2.436388	H	3.466618	-4.241677	1.818985
H	-4.109290	2.527348	-2.709743	H	1.905336	-4.829907	-2.163193
H	2.387627	4.151091	3.001364	H	3.898968	-2.936798	2.918385
C	-4.199865	0.385555	-2.579792	H	-0.145769	1.417184	4.352611
C	2.762368	2.034321	2.890817	C	-3.728513	-1.734868	0.479222
H	-4.635814	0.250411	-3.567130	O	3.659326	-0.150258	-0.924645
H	3.327149	2.019064	3.822778	C	3.878453	0.704785	-1.869292
C	-4.060797	-0.713633	-1.722574	C	5.351004	0.749286	-2.255869

H	5.511588	1.495665	-3.039823
H	5.961969	0.991504	-1.378506
H	5.671266	-0.237532	-2.609765
O	3.057171	1.424256	-2.431445
F	-2.816220	-2.731180	0.387852
F	-3.765280	-1.350291	1.752632
F	-4.904409	-2.309808	0.209808
C	-2.605230	3.316903	0.928233
H	-2.512875	4.312470	1.361306
C	-3.122171	3.131654	-0.310784
H	-3.447494	3.977860	-0.916138
C	0.386833	4.451658	-0.591230
H	0.013220	5.375306	-1.034046
C	1.011923	4.469745	0.619481
H	1.144310	5.412979	1.150795

Structure N

E (BS1) = -2385.23123197 au

H (BS1) = -2384.672605 au

G(BS1) = -2384.786605 au

E(M06/BS2//M06/BS1, Solvent = CH_2Cl_2) = -2388.25288698 au

E(BP86/BS2//M06/BS1, Solvent = CH_2Cl_2) = -2389.83428484 au

E(TPSS/BS2//M06/BS1, Solvent = CH_2Cl_2) = -2389.85873575 au

E(wB97XD/BS2//M06/BS1, Solvent = CH_2Cl_2) = -2388.92963629 au

Pd	0.436421	-1.536464	-0.619550
Pd	-1.649644	-0.189808	0.432044
O	-1.234774	-1.877334	-2.134616
O	-1.522584	-1.738793	1.941679
C	-1.028730	-2.851212	1.607231
O	-0.339528	-3.082992	0.574113
C	-2.408752	-1.935884	-1.741655
O	-2.884688	-1.365005	-0.690129
C	-0.203637	2.241349	0.845926
C	0.118606	0.840872	2.680527
C	0.615985	3.246579	1.381527
C	0.920842	1.811232	3.297288
H	-0.079629	-0.132148	3.125452
C	1.175106	3.002896	2.648809
H	1.352767	1.596363	4.270466
H	1.814559	3.757370	3.107317
C	-1.689806	1.354619	-0.849516
C	-2.392986	1.501392	-2.022685
C	-0.867152	2.401892	-0.395528
C	-2.235124	2.689762	-2.768263
H	-3.075397	0.730743	-2.375577
C	-0.698637	3.590770	-1.134596
C	-1.403477	3.709899	-2.347590
H	-2.789735	2.799369	-3.699345
H	-1.298055	4.617664	-2.941436
C	2.072061	-1.244838	0.605245
C	2.592622	0.079565	0.361531
C	2.172375	-1.703278	1.944557
C	3.428366	0.745376	1.291158
C	2.946467	-1.006306	2.866703
H	1.773148	-2.684553	2.196925
C	3.616500	0.178980	2.557559

H	3.056419	-1.430221	3.866312
H	4.255999	0.671197	3.289595
C	0.934203	0.614364	-2.773333
C	2.245348	0.709644	-0.846008
C	1.508242	1.791351	-3.261006
H	0.155213	0.078751	-3.314461
C	2.827169	1.937739	-1.244974
C	2.433321	2.466337	-2.478907
H	1.180726	2.187311	-4.218806
H	2.855798	3.414507	-2.814378
O	1.713949	-3.062985	-1.872449
C	2.805150	-3.044866	-1.300476
O	3.111433	-2.329693	-0.265140
C	-1.240393	-4.002896	2.553712
H	-1.095124	-4.959025	2.043782
H	-0.500025	-3.925917	3.361441
H	-2.235227	-3.949481	3.005736
C	-3.412264	-2.742103	-2.523392
H	-3.244864	-3.804192	-2.307130
H	-4.440052	-2.483045	-2.256029
H	-3.241824	-2.597040	-3.595150
C	3.944180	-3.916185	-1.769070
H	4.865191	-3.329250	-1.848129
H	4.121990	-4.702791	-1.026273
H	3.699594	-4.374520	-2.730823
N	-0.422202	1.067189	1.492072
N	1.269683	0.111210	-1.590377
C	-3.420559	0.601875	1.246227
F	-3.187081	1.711421	1.959547
F	-4.331694	0.895824	0.322879
F	-3.942438	-0.306660	2.060470
C	0.806942	4.431404	0.598606
C	0.180604	4.591905	-0.601160
H	1.465517	5.206906	0.989057
H	0.333387	5.504518	-1.177774
C	4.000383	1.999225	0.882781
C	3.737604	2.559259	-0.330585
H	4.668319	2.504850	1.582287
H	4.194236	3.507201	-0.617205

Structure O

E (BS1) = -2385.26151169 au

H (BS1) = -2384.699852 au

G(BS1) = -2384.816555 au

E(M06/BS2//M06/BS1, Solvent = CH_2Cl_2) = -2388.28617677 au

Pd	-0.014502	-1.521478	0.674627
Pd	1.744487	0.049480	-0.519921
O	2.246077	-0.899853	2.513061
O	1.903887	-1.680596	-1.845372
C	1.732797	-2.811016	-1.307279
O	1.092752	-3.028364	-0.242184
C	3.208985	-1.056169	1.771833
O	3.309154	-0.699411	0.524070
C	-0.301882	1.980565	-1.096719
C	-0.518391	0.197817	-2.578333
C	-1.396730	2.664855	-1.654250
C	-1.620815	0.811383	-3.184065
H	-0.125367	-0.767366	-2.893164
C	-2.063496	2.036251	-2.718498

H	-2.125120	0.305606	-4.003122
H	-2.928838	2.521259	-3.172009
C	1.509873	1.755506	0.502750
C	2.261435	2.264742	1.539299
C	0.436509	2.511759	-0.009550
C	1.921910	3.522232	2.076982
H	3.109367	1.713694	1.937829
C	0.088613	3.771867	0.523446
C	0.860646	4.264702	1.590290
H	2.520843	3.918938	2.896092
H	0.622465	5.237529	2.020817
C	-3.159699	-1.769901	0.050972
C	-3.206712	-0.360729	0.259866
C	-3.898566	-2.372785	-0.951721
C	-4.198007	0.358900	-0.467903
C	-4.755108	-1.606373	-1.751019
H	-3.828409	-3.443287	-1.093568
C	-4.933122	-0.269596	-1.490382
H	-5.321796	-2.097375	-2.539915
H	-5.660751	0.319722	-2.048137
C	-0.552499	0.563313	2.637124
C	-2.387824	0.387396	1.201501
C	-1.026173	1.752957	3.199553
H	0.410359	0.142360	2.927537
C	-2.815573	1.683622	1.593801
C	-2.126696	2.341009	2.627863
H	-0.468817	2.230256	4.001138
H	-2.472902	3.325458	2.945704
O	-2.142433	-4.427438	-0.179554
C	-1.994016	-3.777922	0.818500
O	-2.475288	-2.499207	1.000524
C	2.371929	-3.992934	-1.985662
H	1.916566	-4.931407	-1.658119
H	2.302479	-3.889036	-3.073121
H	3.438293	-4.004253	-1.726672
C	4.475983	-1.735686	2.249120
H	4.555977	-2.719528	1.770586
H	5.359574	-1.159641	1.954248
H	4.447586	-1.864256	3.334601
C	-1.265164	-4.202121	2.054152
H	-0.294856	-3.682027	2.096606
H	-1.825962	-3.928725	2.954056
H	-1.087552	-5.279390	2.015811
N	0.108626	0.773774	-1.560552
N	-1.193759	-0.085661	1.665025
C	3.196564	1.118537	-1.624085
F	2.643091	2.086810	-2.375898
F	4.125782	1.692991	-0.857677
F	3.817861	0.279434	-2.447505
C	-1.744827	3.934276	-1.087030
C	-1.031780	4.460600	-0.052846
H	-2.596001	4.470935	-1.506306
H	-1.306639	5.431798	0.360584
C	-4.501258	1.715767	-0.130051
C	-3.889386	2.328815	0.909410
H	-5.282950	2.219534	-0.699084
H	-4.159892	3.340281	1.212762

Acetate

E (BS1) = -228.372381147 au

H (BS1) = -228.318464 au

G(BS1) = -228.350668 au

E(M06/BS2//M06/BS1, Solvent = CH_2Cl_2) = -228.565351316 au

E(BP86/BS2//M06/BS1, Solvent = CH_2Cl_2) = -228.701437827 au

E(TPSS/BS2//M06/BS1, Solvent = CH_2Cl_2) = -228.721606582 au

E(wB97XD/BS2//M06/BS1, Solvent = CH_2Cl_2) = -228.617441167 au

C	-0.219624	0.001877	-0.005648
C	1.342794	-0.057158	-0.002116
H	1.751252	0.595096	-0.788730
H	1.724111	0.335116	0.953796
H	1.723657	-1.079441	-0.138447
O	-0.687501	1.162706	0.001194
O	-0.804754	-1.102591	0.001301

Water

E (BS1) = -76.3738331110 au

H (BS1) = -76.348480 au

G(BS1) = -76.369910 au

E(M06/BS2//M06/BS1, Solvent = CH_2Cl_2) = -76.4260659962 au

O	0.000000	0.000000	0.118339
H	0.000000	0.760840	-0.473357
H	0.000000	-0.760840	-0.473357

Structure from inflexion on increasing $Pd_a \cdots Pd_b$ in cation A

(optimized by M06/BS1)

E (BS1) = -2156.69969139 au

H (BS1) = -2156.194560 au

G (BS1) = -2156.301071 au

E(M06/BS2//M06/BS1, Solvent = CH_2Cl_2) = -2159.67031263 au

Pd	2.004050	-0.607388	-0.495913
Pd	-1.830983	-0.796201	-0.086022
N	2.762527	1.285983	-0.868439
N	-2.078209	0.482627	1.498288
C	2.196355	2.296174	-1.518759
C	-1.513294	0.395494	2.696840
H	1.199601	2.117843	-1.918662
H	-0.883386	-0.475090	2.871591
C	2.848777	3.524443	-1.682835
C	-1.732878	1.394532	3.653717
H	-1.264529	1.301133	4.629416
C	4.115565	3.698122	-1.158621
C	-2.540614	2.474174	3.348255
H	4.638518	4.646670	-1.278141
H	-2.718118	3.253161	4.088914
C	4.737115	2.642975	-0.469321
C	-3.139989	2.573587	2.078776
C	6.046045	2.688874	0.113581
C	-3.993770	3.636609	1.634945
H	6.619290	3.611172	0.029904
H	-4.205712	4.452866	2.323534
C	6.567181	1.605383	0.754479
C	-4.535111	3.628964	0.384122
H	7.565773	1.658395	1.187527
H	-5.186284	4.443237	0.068779
C	5.836769	0.376111	0.878485
C	-4.277778	2.565941	-0.545214
C	6.323315	-0.782013	1.515722
C	-4.825920	2.478289	-1.841461
H	7.318242	-0.773246	1.959104
H	-5.491753	3.264538	-2.194182

C	5.543998	-1.920976	1.568602	O	-0.032399	-0.252198	-1.523011
C	-4.536662	1.400110	-2.653497	C	0.388581	-2.780063	0.548761
H	5.934066	-2.812782	2.057058	C	-0.435830	-1.242638	-2.204744
H	-4.979994	1.340226	-3.645748	C	-0.088103	-4.191525	0.728336
C	4.249974	-1.969829	1.002772	C	0.299253	-1.751039	-3.393314
C	-3.680163	0.353271	-2.233484	H	-0.938539	-4.354411	0.050007
H	3.665085	-2.886170	1.050897	H	1.039826	-2.486134	-3.049515
H	-3.477611	-0.493375	-2.886147	H	0.691841	-4.919335	0.492610
C	3.751635	-0.846478	0.383095	H	-0.380706	-2.251338	-4.088733
C	-3.131931	0.447511	-0.982958	H	-0.459337	-4.337131	1.748211
C	4.544377	0.317270	0.318575	H	0.834859	-0.935602	-3.888901
C	-3.424679	1.524096	-0.130036	H	2.349651	4.324455	-2.222882
C	4.010394	1.444873	-0.349461	C	-3.427939	-1.863840	0.573105
C	-2.874392	1.535036	1.173054	F	-4.404236	-1.119300	1.050097
O	1.445409	-2.588383	-0.111540	F	-3.859050	-2.571511	-0.448174
O	-1.499773	-1.848053	-1.826771	F	-2.986619	-2.662741	1.523503
O	-0.310060	-1.841732	1.048510				

Basis Set Comparison for Transition State Energies

Relative energies (kcal mol^{-1}) calculated for four density functionals for reaction coordinate analyses in Schemes 5 and 6; energy (enthalpy).

	M06	BP86	TPSS	wB97XD
C (TS for fragmentation from **B**)	13.7 (13.0)	19.5 (18.4)	2.7 (1.6)	15.9 (14.9)
J (TS for C–C from **A**)	18.4 (28.3)	25.3 (35.2)	10.3 (20.1)	22.3 (32.1)
L (TS for C–C from **B**)	18.9 (19.3)	21.8 (22.1)	5.2 (5.5)	26.6 (27.0)
N (TS for C–O from **B**)	23.5 (22.5)	23.0 (22.0)	7.3 (6.26)	29.4 (28.3)

Functionals BP86, TPSS and wB97XD were chosen to represent three different classes of functional (rungs 2, 3, and 4, respectively on Jacob's ladder; M06 is rung5). Although the results for TPSS are broadly consistent trends with the other functionals, TPSS is reported to be not as good as M06 for computing reaction barriers (Karton, A.; Tarnopolsky, A.; Lamére, J-F.; Schaltz, G. C.; Martin, J. M. L. *J. Phys. Chem. A* **2008**, *112*, 12868), and that TPSS gives the least accurate bond dissociation energies (Cramer, C. J.; Truhlar, D. G. *Phys. Chem. Chem. Phys.* **2009**, *11*, 10757). It seems possible that the poor performance of TPSS might be representative of the "meta generalized gradient approximation" functionals, i.e. the third rung of Jacob's ladder.

Full citation for reference 20

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[ix] Treatment of **1** with XeF_2 followed by AcOH and then $TMSCF_3$ results in the formation of Pd(III) tetraacetate complex **3**; no Pd(IV) complex **5** could be observed when this order of addition was executed. In addition, if binuclear Pd(III) tetraacetate complex **3**, prepared as outlined above, is treated with $TMSCF_3$, no reaction to produce **5** was observed.

[x] Analogous conditions (XeF_2 and TMSX) have been employed in the synthesis of compounds **2** and **3** (see above). Synthesis of **9** by the aforementioned procedure can afford mixtures of compounds **9** and **1**; in some iterations, a 1:1 mixture of **9** and **1** were observed while in others, **9**, free of **1** was observed by ^{1}H NMR spectroscopy.

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[xii] AcOH, not OAc^-, catalyzes the oxidation of **1** to **5**. No reaction was observed upon treatment of **1** with 3.0 equiv **4** in the presence of 2.0 equiv nBu$_4$NOAc for 13 h at 23 °C.

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